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# (54) TWO-COMPONENT DEVELOPER, DEVELOPING METHOD AND IMAGE FORMING **METHOD**

# (57)Abstract:

PROBLEM TO BE SOLVED: To form a toner image of high image quality while preventing or supporting deposition of a carrier and production of fog by specifying the constitution of the carrier and the toner.

SOLUTION: The carrier used is a resin-coated magnetic carrier having such distribute of particle size that the number average particle size ranges 1 to  $100 \mu m$  and that the cumulative value of particles having ≤1/2 of the number average particle size is ≤20%. The carrier has 1× 1012Ωcm specific resistance in 5×104V/m electric field and shows 40 to 220emu/cm3 magnetization in 1kOe magnetic field. The toner has such properties that the distribution of particle size shows 0.5 to 10.0µm number average particle size, ≤10% cumulative value of particles having ≤1/2 particle size of the average particle size (D1, ≤10% cumulative value of volume of particles having ≥2 times diameter of the volume average particle size (d3), ≤20% coefft. of valiation in the particle size distribution based on the number, and 100 to 140 shape coefft. SF-1. In the mol.wt. distribution by GPC of the THF-soluble component, the proportion of the component having ≤1000mol.wt. is ≤10wt.% based on the toner weight.

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### DETAILED DESCRIPTION

# [Detailed Description of the Invention] [0001]

[The technical field to which invention belongs] this invention relates to the development method and the image formation method using the binary system developer and this binary system developer for developing the electrostatic latent image in a xerography, an electrostatic recording method, etc. [0002]

[Description of the Prior Art] Various methods are indicated by a U.S. Pat. No. 2,297,691 specification, JP,42-23910,B, JP,43-24748,B, etc. about the xerography. These methods all form an electrostatic latent image on a photo conductor by irradiating the light figure according to the manuscript at a photoconduction layer. subsequently After making the coloring impalpable powder called toner which has polarity with this opposite on this electrostatic latent image adhere, developing an electrostatic latent image and imprinting a toner picture on imprinted material, such as paper, if needed, it is established with heat, a pressure, or a solvent steam, and a duplication is obtained.

[0003] In process in which an electrostatic latent image is developed, toner image formation is performed on an electrostatic latent image using the electrostatic interaction of the electrified toner particle and an electrostatic latent image. Generally, when developing this electrostatic latent image using a toner, the binary system developer which made the medium called carrier distribute a toner in the full color copying machine of which high definition is required especially is used suitably. [0004] Moreover, by development of recent years, a computer, multimedia, etc., a means to output a still higher definition full color picture is demanded, and it gets down, and a copy picture full color for this purpose is further made into high definition and high brilliance, especially, the dot repeatability of the halftone section is raised, gradation nature is raised, and the efforts improved in quality even to the picture level of a silver salt photograph are made. According to such a demand, various examination is added from a viewpoint of a development process and the charge of development material. [0005] For example, about a developer, the method of making small particle size of the toner which is the component of a binary system developer, and a carrier as the typical thing can be mentioned. However, in addition to the problem on the handling of fine particles generating diameter-ization of a granule of a toner, it becomes difficult with minor-diameter-izing of toner particle size to optimize [ of the electrophotography property in imprint process, fixing process, etc. other than development process ]. For this reason, there is a limitation only in the viewpoint referred to as attaining high definition-ization by the toner independent.

[0006] On the other hand, in examination of an electrophotography process, possibility of attaining high definition-ization can be mentioned by making the development brush on a development sleeve dense. As the method of dense-izing of the development brush from a process side, the method of a development sleeve magnetic pole of developing negatives in between very much, the method of making small the strength of magnetic pole of a development sleeve, etc. can be considered, for example. According to these methods, although it is hard coming to receive the influence of a magnetic brush, it is difficult for there to be also a problem in the one side and the field of scattering by the

shortage of restraint of a developer or conveyance nature, and to adopt simply.

[0007] Dense-ization of a magnetic brush is attained also by making small particle size of the carrier particle used for a binary system developer, or decreasing a magnetic force. For example, the method of using the small carrier of saturation magnetization for JP,59-104663,A is indicated. However, although improvement in the repeatability of a thin line can be aimed at when the small carrier of saturation magnetization is used simply, it is one side, and in order that the restraint of the carrier particle on a development sleeve may decline, it becomes easy to generate the so-called carrier attachment phenomenon which a carrier shifts on a photoconductor drum and generates a picture defect. In addition, the bird clapper is known that it is easy to generate this carrier attachment phenomenon also by using the carrier of the diameter of a granule.

[0008] The method of developing by the non-contact method under oscillating electric field to JP,5-8424,B as a cure to this carrier attachment phenomenon using the carrier and toner which atomized is indicated. In order to improve carrier adhesion in the development process which impresses oscillating electric field to the official report concerned, high resistance-ization of a carrier is indicated to have an effect. However, the specific resistance of the carrier core which constitutes the carrier though specific resistance of a carrier is formed into high resistance in order to improve generating of carrier adhesion was low, and, in the case that the core is more nearly exposed to a front face etc., that carrier adhesion is improved and high definition-ization is attained had the case of being difficult. Moreover, although according to this method the picture which does not produce the carrier adhesion which has the picture concentration of there there, either is acquired when the intensity of magnetization of the carrier in a development pole is large since the non-contact method is adopted, especially when the intensity of magnetization of a carrier becomes small, the problem that picture concentration becomes low is also produced.

[0009] By the way, with it being general, on the distributed resin carrier which distributed the magnetic substance in the resin, since the bulk resistor of a carrier becomes high compared with the carrier which consists only of an iron powder metallurgy group oxide (for example, a ferrite, a magnetite core), it is thought that it is effective as a means for improving carrier adhesion. As [ indicate / by JP,5-100494,A /, for example / however, / by these cases ] Although it becomes high as restraint of a magnetic carrier when a magnetic particle which made the quantity of the amount of magnetic substance in a resin increase by making two or more magnetic substance with which particle-size ratios differ contain is used as a resin carrier into a resin, and the low magnetic substance of specific resistance is inner-\*\*(ed) in the magnetic substance When such a carrier was especially used for the development method using an alternating electric field etc., there was a case where carrier adhesion was not fully improvable. [0010] The transfer picture is fixed, after developing an electrostatic latent image with the developer made to support on a developer support and imprinting the acquired toner picture to imprinted material, in using conventionally the binary system developer which mixed the toner and the carrier and was prepared. In this process, in case a developer is made to support on a developer support, in order to make a moderate uniform developer layer form on a developer support, usually, specification-part material is arranged to the development counter, and the uniform development layer is formed by this specificationpart material.

[0011] However, when the binary system developer which consists of a toner obtained by the direct polymerization method and a carrier was contained and used for the development counter which specification-part material possesses, since the fluidity of a developer was very good, as compared with the case where the binary system developer which consists of a toner obtained by the conventional grinding method and a carrier is used, there was a case where the phenomenon in which a developer passes through between a developer support and specification-part material occurred. For this reason, that uniform coating is not obtained arose that the amount of electrifications between developer particles tends to become uneven, and there was a case where a poor picture with ground fogging or picture nonuniformity occurred. Furthermore, although a developer support body surface has a mirror-plane configuration, since the developer supported on a developer support for the conveyance lack of ability to a hoop direction produces a bias [ near the ends of a developer support ] in a case, a developer enters

into a bearing etc. in the copy durability of a repeat and the weld object of a developer is generated, it is easy to cause a poor imprint at the time of an imprint, and becomes the cause of a picture defect.

[0012] Moreover, as a result of being easy to carry out packing of the toner generally obtained by the direct polymerization method within a development counter since it has a globular form configuration substantially, filling up densely a part for the specification-part material downstream in a development counter with a developer and being strongly pushed against a developer support depending on the case, the so-called sleeve contamination which a developer welds to a sleeve front face occurs. This sleeve contamination becomes the cause of the fall of picture concentration, and ground fogging and is not desirable. In the developer using the grinding method toner which contains a lot of low softening temperature matter especially, this phenomenon becomes remarkable.

[0013] In JP,63-247762,A, the application which used for the developer the toner obtained to the monomer by 50 or the direct polymerization method which carried out 3,000 weight sections content in low softening temperature matter, such as paraffin, and paid its attention to the surface roughness (Rzmax value) of a developer support is made. However, according to this method, although the effect in the early stages of copy durability of a repeat was accepted about weld of a up to [ the developer support of a developer ], after the copy durability of a repeat, the case where toner weld occurred was on the developer support. Moreover, it was difficult to be stabilized and to continue conveying a fluid good developer which was described above on a developer support only by regulation of sleeve surface roughness (Rzmax value).

[0014] Although the various technique for attaining high definition-ization is tried preventing carrier adhesion as mentioned above, the present condition is that the means which can solve all the faults of the conventional technology expressed previously is not acquired the place by present.

[0015]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the development method and the image formation method of using the binary system developer which solved all the troubles of the above-mentioned conventional technology, and this binary system developer. That is, the purpose of this invention has carrier adhesion and generating of fogging in offering the development method and the image formation method of using the binary system developer which can form the high definition toner picture prevented or suppressed effectively, and this binary system developer. Moreover, the purpose of this invention is to offer the development method and the image formation method of using the binary system developer which can form the color toner image which was excellent in high picture concentration at high brilliance and gradation nature, and this binary system developer. moreover, the purpose of this invention -- the life of a developer -- extending -- many -- it is in offering the binary system developer which does not have picture degradation after the copy of several sheets Moreover, the purpose of this invention is in an improvement of the durable property of repeat use, and is to offer the binary system developer which does not produce filming on a photo conductor. Furthermore, the purpose of this invention is to offer the stable image formation method which does not produce developer weld on a developer support. [0016]

[Means for Solving the Problem] The above-mentioned purpose is attained by the following this invention. Namely, this invention is set to the binary system developer which has a toner and a magnetic carrier at least. The above-mentioned carrier is a resin coat magnetism carrier to which the coat of the carrier core particle front face which has a binder resin and a metallic oxide was carried out with the resin. And the number distribution accumulation value below the diameter of 1-/double precision of the number mean particle diameter 1 or 100 micrometers, and a number mean particle diameter has 20-piece several% or less of particle size distribution. The specific resistance in the field strength of 5x104 V/m Furthermore, more than 1x1012-ohmcm The intensity of magnetization in a 1K oersted is 40 or 220 emu/cm3. And the above-mentioned toner has the binding resin 100 weight section, a coloring agent 0.1, or 15 weight sections at least. The number distribution accumulation value below the diameter of 1-/double precision of 0.5 or 10.0 micrometers, and this number mean particle diameter (D1) Several 10% or less, [ the number mean particle diameter of this toner ] The volume-integral cloth accumulation

value more than the diameter of double precision of a volume mean particle diameter (D3) Below 10 volume % In molecular weight distribution the coefficient of variation of the particle size distribution of number criteria is 20% or less, and shape factor SF-1 is 100 or 140 further, and according to GPC of a THF meltable component The content of a with a molecular weight of 1,000 or less component is the binary system developer which is 10 or less % of the weight, and is characterized by the maximum peak (Mp) of molecular weight being in molecular weight 3,000 or the field of 100,000 on the basis of the weight of a toner.

[0017]

[The mode of implementation of invention] Hereafter, the mode of operation of this invention is mentioned and this invention is explained in detail. When this invention persons perform detailed examination that the trouble of the above-mentioned conventional technology should be solved, first as a carrier which constitutes a binary system developer Intensity-of-magnetization sigma1000 in a development pole (strength of magnetic pole about 1,000 oersteds) by 40 or 220 emu/cm3 And when the number mean particle diameter used the magnetic carrier in the range which is 1 or 100 micrometers, it turns out that the density of the developer MAG brush in a development pole becomes dense, and a picture with sufficient dot repeatability is acquired.

[0018] However, when the magnetic carrier with which are satisfied of the above-mentioned physical properties is used, it also turns out that there is an inclination to disagree with improvement in quality of image, and for carrier adhesion to increase. Then, as a result of repeating examination further, it sets to this invention. In addition, as the distribution accumulation value below the diameter of 1-/double precision of a number mean particle diameter becomes several 20% or less, the particle size distribution of a magnetic carrier are made sharp, a number mean particle diameter is 1 or 100 micrometers -- And substantial high resistance-ization of a magnetic carrier is attained by carrying out specific resistance of the magnetic carrier in the field strength of 5x104 V/m to more than 1x1012-ohmcm. The improvement in quality of image is made to attain by using on it the magnetic carrier whose intensity of magnetization in a 1K oersted is 40 or 220 emu/cm3, preventing carrier adhesion.

[0019] Furthermore, when it was made for the specific resistance of the carrier core particle (the portion which has the magnetism in a magnetic carrier is meant hereafter) which constitutes a magnetic carrier to become more than 1x1010-ohmcm in addition to the above-mentioned conditions, it turns out that carrier adhesion is prevented more effectively. Especially this is set to the contact development method that the driving force of carrier adhesion develops negatives by impressing an alternating electric field to a development support, and is considered because charge pouring to a magnetic carrier from the development sleeve at the time of development bias impression serves as a dominant factor. Namely, the carrier adhesion produced in the case of charge pouring Even if a carrier is a resin coat magnetism carrier (it is only hereafter called a coat magnetism carrier) which made the carrier core particle front face cover a resin When the specific resistance of a carrier core particle like a metal iron core, a magnetite core, or a ferrite core uses the particle which is below 9x108-ohmcm If these carrier core particles expose that it is also partial to a magnetic carrier front face, charge pouring to a carrier will take place, and it is thought that carrier adhesion is produced. Moreover, when the distributed resin carrier which distributed the magnetic substance in the resin was used as a carrier core and a resin carrier [ as / whose specific resistance of this carrier core particle is under 1x1010ohmcm ] was used, it traced that charge pouring to a carrier took place.

[0020] Moreover, it also turns out that there is electrification of the magnetic carrier in the triboelectrification between a toner / magnetic carrier as a factor of other carrier adhesion. That is, although it is rare to produce an attachment phenomenon in a photo conductor with the magnetic force and self-weight when the magnetic electrified carrier has a large particle size, the particle size distribution of the particle size of a magnetic carrier are broadcloth, and since the magnetic carrier with a small particle size may fly to up to a photo conductor and may produce adhesion, when the magnetic carrier with which especially fines are contained so much is used, increase of the coating weight of a carrier produces it.

[0021] Therefore, in order to have prevented carrier adhesion effectively, this invention persons

prevented charge pouring to a magnetic carrier, when the specific resistance of a carrier core particle raised the bulk resistor of a carrier core particle as a magnetic carrier using a magnetic high carrier, and when using the magnetic carrier which has the particle size distribution in the state where the fines portion was cut, they thought further that the problem of carrier adhesion was solved.

[0022] However, when the conventional resin carrier which can prevent the carrier adhesion by charge pouring to a magnetic carrier as a result of continuing examination further was used and it used for the carrier front face, without giving a coat, it turns out that the amount control of electrifications to various toners may not work. Moreover, when there were few contents of the magnetic substance contained in the carrier, the reason had the case where the triboelectrification grant to a toner became unstable, although it was not certain.

[0023] Then, this invention persons also thought that it became possible to perform the amount grant of electrifications to a toner good while being able to prevent carrier adhesion effectively, when giving and using the resin coat for this carrier core particle as a magnetic carrier using the carrier core particle of high resistance so that charge pouring to a carrier could be prevented.

[0024] and as composition of the magnetic carrier with which it can be [ both ] satisfied of especially electrification nature and carrier antisticking good If a part of magnetic-substance particle is replaced by the metallic oxide with a big particle size and it is used by high resistance rather than it in order to attain high resistance-ization of a carrier core, making a metallic oxide contain so much The rate of the metallic oxide/binder near [ apparent ] the carrier front face could be made small, consequently I could make the bulk resistor of a magnetic carrier high, and thought that prevention of carrier adhesion was made by this with high definition-ization.

[0025] Here, in the magnetic carrier which was made to carry out direct polymerization of a resin and the metallic oxide, and manufactured them especially, it turns out that a big metallic oxide pulls out the head on a magnetic carrier front face mostly, and exists in it. Moreover, the large drop child found out the bird clapper that it is easy to pull out the head on a front face, so that the particle-size ratio of a resin and a metallic oxide was large. Therefore, if the high resistance metallic oxide with a big particle size is introduced on the occasion of manufacture of a magnetic carrier, it will be thought that the bulk electric resistance of a carrier core can be raised more. Furthermore, since the coat of the various resins can be carried out to a carrier core front face good, without restricting the carrier core particle formed to the coat methods, such as a wet method or dry process, if a hardened type resin is used as a binder, when manufacturing a carrier core particle with a metallic oxide and a binder resin and it can perform easily considering as the resin carrier which has good electrification grant ability to a toner, it is still more desirable.

[0026] Moreover, in this invention, it is using the resin coat magnetism carrier of composition of using it by this invention, and it is thought that dot repeatability can be raised more according to the factor described below. First, although one of the causes of degradation, such as a dot, is presumed because the digital static latent image of the shape of a dot of the neighborhood where the charge was leaked had become an uneven configuration as a result of being leaked, when the magnetic carrier of low resistance [ the latent-image charge of photo conductor drum lifting ] \*\*\*\* conventionally On the magnetic carrier used by this invention, it thinks because producing disorder of the electrostatic latent image by the above factors is lost by raising the specific resistance of the carrier core particle which constitutes the magnetic carrier. In the binary system developer of this invention, namely, by making the intensity of magnetization of the magnetic carrier in a 1K oersted into 40 or 220 emu/cm3 The density of the developer MAG brush in a development pole by the thing which are made dense and which the bulk resistor of a carrier core is raised and is simultaneously omitted for the fines portion in a magnetic carrier It becomes possible to develop negatives, without preventing charge pouring to a carrier effectively, consequently disturbing an electrostatic latent image, and it is thought that a high-definition picture is formed more.

[0027] However, in order to acquire the toner [ which is the purpose of this invention ] picture which was highly minute and was excellent in gradation nature, not only improvement of the above-mentioned resin carrier but improvement of a toner is important. Hereafter, the toner used by this invention is

explained. As a toner for constituting a binary system developer combining the above-mentioned resin carrier used in this invention 0.1 or 15 weight sections contain [ the coloring agent ] to the binding resin 100 weight section at least. The number mean particle diameter of this toner is 0.5 or 10.0 micrometers. the number distribution accumulation value below the diameter of 1-/double precision of a number mean particle diameter (D1) Several 10% or less, The volume-integral cloth accumulation value more than the diameter of double precision of a volume mean particle diameter (D3) Below 10 volume % In molecular weight distribution the coefficient of variation of the particle size distribution of number criteria has 20% or less of sharp particle size distribution, and the configuration of a toner is [ shape factor SF-1 ] 100 or 140 further, and according to GPC of near and a THF meltable component to a globular form On the basis of the weight of a toner, the content of a with a molecular weight of 1,000 or less component is 10 or less % of the weight, and uses the toner which has the maximum peak (Mp) of molecular weight in molecular weight 3,000 or the field of 100,000.

[0028] In this invention, it is using together the magnetic carrier which has the sharp particle size distribution into which the fines which described it as the sharp toner previously were cut, and there is no fogging and the formation of a picture with sufficient dot repeatability of such particle size distribution is attained. That is, when triboelectrification of a toner and the magnetic carrier is first carried out [1st] by using the toner which has the above properties, the particle size distribution of a toner are sharp, and since the toner configuration is brought further close to a globular form, it becomes possible to make a toner TORIBO distribution sharp. Furthermore, in this invention, since the particle size of the magnetic carrier which carries out electrification grant is equal to the toner with this, the opportunity of contact on a toner and a carrier becomes equal, and is considered that electrification grant to a more uniform toner is performed these results. Since a toner TORIBO distribution becomes sharp and existence of the toner of a reversal component has actually become the minimum when the binary system developer of this invention is used, the development by the toner faithful to a latent-image charge is attained. Furthermore, it is thought that the toner used in this invention becomes geometrically advantageous compared with the case where an indeterminate form toner is used when it is considered that development is concealment of the latent-image charge by the toner particle, since it was a globular form substantially, and does not have fogging, and a picture with sufficient dot repeatability is acquired. Moreover, that the toner used in this invention tends to be charged uniformly, since it is a globular form geometrically, it is thought that it excels also in the imprint nature from a photo conductor to imprinted material, there is no fogging, and a picture with sufficient dot repeatability is acquired. [0029] Furthermore, with the binary system developer which has the same property and which combined the carrier with sharp particle size distribution, and the toner of the configuration near a globular form with sharp particle size distribution, that it is filled up only densely within a development counter, and is easy to produce packing turned out to have described above. And the share at the time of this packing and the share in the portion which regulates the developer MAG brush in a development counter became a cause, and the external additive on the front face of a toner was buried after several multi-sheet durability, and it turns out that the so-called toner SUPENTO which a toner resin welds to a carrier front face may arise. Furthermore, since the degradation toner and carrier which received such a damage are inferior in electrification capacity, development nature gets worse and they become causes, such as fogging and toner scattering. Moreover, the degradation toner from which the external additive was buried or it was desorbed causes picture defects, such as a toner white omission, when not only development nature but imprint nature is bad, tends to become an imprint remains toner on a photo conductor and is imprinted by imprinted material. Since a contact opportunity with a carrier increases inevitably especially when a toner is close to a globular form, it is for external additives, such as a silica adhering to the front face, to be buried, or to \*\*\*\* etc. in the inclination to be easy to deteriorate. [0030] Then, at the two component developer of this invention, it is intensity of magnetization [ in / the 1K oersted of a magnetic carrier / first ] 40 or 220 emu/cm3 Remarkable mitigation of toner degradation after several above-mentioned multi-sheet durability and toner SUPENTO to a carrier was able to be carried out by using a resin carrier with specific gravity smaller than carriers, such as making it low, and conventional iron powder, a ferrite carrier. This is considered that it is a reason that the magnetic share

which works between the toner within a development counter and carriers or on carriers, and a weight-share can be lessened by controlling as mentioned above.

[0031] Furthermore, in addition to the composition of the resin carrier which suppressed such magnetization, in the molecular weight distribution by GPC of the THF extractives of a toner, a problem which described above the content of a with a molecular weight of 1,000 or less component by stopping to 3 or less % of the weight still more preferably 5 or less % of the weight preferably was further mitigable in this invention 10 or less % of the weight. That is, the component of the low molecular weight whose molecular weight in the THF extractives of a toner is 1,000 or less will be considered because it is set to one of the causes of many problems at the time of packing which was described above if many such low molecular weight constituents are contained in order to work in the direction which plasticizes the whole toner.

[0032] If average molecular weight of the THF extractives of a toner is made high too much in order to \*\*\*\* the content of a with a molecular weight [ in the THF extractives in a toner ] of 1,000 or less low molecular weight constituent to 10 or less % of the weight, since the softening temperature of a toner rises, the fixing temperature of a toner must be raised, the wait time of a copying machine or a printer will rise or power consumption will become high on the other hand, it is not desirable. In the toner used by this invention, in order to stabilize fixing nature and shelf life, the maximum peak of the molecular weight distribution in the THF extractives of a toner uses the thing in molecular weight 3,000 or the field of 100,000. About the concrete method for obtaining the toner of such molecular weight distribution, it mentions later.

[0033] In this invention, by a magnetic carrier and particle size distribution with sharp particle size distribution being sharp, and using the toner of the configuration near a spherical diameter as mentioned above Development faithful to the electrostatic charge which makes a toner TORIBO distribution sharp and does not have fogging is attained. It solves by making the magnetic force of a magnetic carrier low for the problem of degradation of the developer by the packing within the development counter which becomes easy to produce with the configuration of this carrier and a toner, and lessening the content of the low molecular weight constituent in the THF extractives of a toner.

[0034] That moreover, the image formation stabilized without producing developer weld on the developer support which is one of the features of the image formation method of this invention becomes possible By making the binary system developer of this invention which consists of a toner which is excellent in a fluidity, and a magnetic carrier support with a globular form substantially on the developer support which specified the shape of surface type especially, and raising the conveyance force of a developer The developer between a developer support and specification-part material passes through, and prevention is attained, and stay of the developer in a specification-part material lower stream of a river is received. Giving a fluidity to a developer by churning operation and the low molecular weight constituent contained among a toner are reduced, and it thinks because weld with the developer support body surface by the packing of a developer is suppressed also by making the intensity of magnetization of a carrier low.

[0035] Hereafter, the material which constitutes the binary system developer of this invention is explained in detail. Although the binary system developer of this invention consists of a magnetic carrier and a toner at least, it explains first the magnetic carrier which can be used by this invention. Although it is desirable from a viewpoint of high-definition-izing to make it as small as possible as for the particle size of the magnetic carrier which constitutes the binary system developer of this invention, if it is made small too much, the problem of carrier adhesion will arise by relation between magnetization and particle size. Therefore, although it is a diameter carrier of a granule and what has the number mean particle diameter within the limits of 1 or 100 micrometers can be used as a magnetic carrier used by this invention from this viewpoint Especially, it is suitable from a viewpoint of high definition, carrier antisticking, and the developer degradation prevention by durability that the intensity of magnetization in the 1K oersted of a magnetic carrier is 40 or 220 emu/cm3, and it is the range whose number mean particle diameter of a carrier is 25 or 80 micrometers. If carrier particle size exceeds 100 micrometers, since it will sweep when a magnetic brush \*\*\*\* a photo conductor front face and will become easy to

produce an eye, it is not suitable from a high-definition viewpoint. Moreover, if it becomes smaller than 1 micrometer, since the magnetic force of one carrier which it has will become small, it becomes easy to produce carrier adhesion and is not desirable.

[0036] Moreover, an important thing has a distribution accumulation value below the diameter of 1-/double precision of the number mean particle diameter of a carrier in using what has sharp 20-piece particle size distribution which become several % or less on the magnetic carrier used in this invention. If the distribution accumulation value below the diameter of 1-/double precision exceeds several 20%, it is not desirable at the point that carrier adhesion increases or the electrification grant to a toner becomes poor as mentioned above. In addition, about the particle-size measuring method of the carrier fine particles used by this invention, it mentions later.

[0037] Although it requires that the intensity of magnetization in a 1K oersted uses the thing of 40 or 220 emu/cm3 as magnetic properties of the magnetic carrier which can be used for the binary system developer of this invention, it is desirable to use still more suitably a carrier [as / whose intensity of magnetization is the range of 40 or 160 emu/cm3] of a low magnetic force. As point \*\* was carried out, the intensity of magnetization of a carrier is suitably chosen by carrier particle size. although it is related also to carrier particle size if intensity of magnetization exceeds 220 emu/cm3, in order for the density of the development brush formed on the development sleeve in a development pole to decrease, and for ear length to become long and to turn uprightly -- a copy picture top -- sweeping -- producing eye nonuniformity \*\*\*\* -- especially -- many -- picture degradation of the husky part of the halftone by durable degradation of the developer by the copy of several sheets, the nonuniformity of a solid picture, etc. will be caused On the other hand, intensity of magnetization becomes insufficient [the magnetic force of a carrier] in less than three 40 emu/cm, carrier adhesion is produced or toner conveyance nature becomes poor. In addition, in this invention, measurement of magnetic properties was measured using oscillating magnetic field mold magnetic-properties automatic-arrangement-for-recording BHV-30 made from \*\*\*\* Electron. The example of measurement conditions is mentioned later.

[0038] As for the magnetic carrier used with the binary system developer of this invention, it requires that the specific resistance has the resistance more than 1x1012-ohmcm in the field strength of 5x104 V/m. In the specific resistance of under 1x1012-ohmcm, as point \*\* was carried out, carrier adhesion and the reduction in the quality of image of the picture in the development process of an electrostatic latent image are remarkable, and the purpose of this invention called high definition and high brilliance cannot be attained. In addition, about the resistance-measurement method of the magnetic carrier fine particles used by this invention, it mentions later.

[0039] Furthermore, in this invention, it is desirable that the specific resistance of the carrier core particle which constitutes a magnetic carrier which was described above has the resistance more than 1x1010-ohmcm in 5x104v [/m] field strength. It causes carrier adhesion or the fall of dot repeatability and is not desirable, in order for charge pouring to take place or to leak a latent image also in a resin coat magnetism carrier, when a carrier core particle also exposes a part, when the specific resistance of a carrier core particle is under 1x1010-ohmcm.

[0040] As a material of the carrier core particle of the magnetic carrier used by this invention, although a metallic oxide can be used, as such a thing, the ferrite which is the iron system oxide expressed with the general formula of MO-Fe 2O3 which shows magnetism, or MFe 2O4 can be used preferably. Here, Mn, Fe, nickel, Co, Cu, Mg, Zn, Cd, Li, etc. whose M is a divalent or univalent metal ion correspond. Moreover, M can be used as an independent or multiple metal. Specifically, a magnetite, a gamma ferric oxide, a Mn-Zn system ferrite, a nickel-Zn system ferrite, a Mn-Mg system ferrite, Li system ferrite, a Cu-Zn system ferrite, etc. can be mentioned. In this invention, it is cheap and it is more desirable to use the magnetite (Fe 3O4) which does not contain any metals other than iron also in having described above.

[0041] Moreover, as other metallic oxides which can be used by this invention, independent, or the metallic oxide which shows the used magnetism and a nonmagnetic metallic oxide are mentioned in metals, such as Mg, aluminum, Si, calcium, Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Sr, Y, Zr, Nb, Mo, Cd, Sn, Ba, and Pb. As a nonmagnetic metallic oxide which can be used in this invention,

aluminum 203, SiO2, CaO and TiO2, V2O5, CrO5, MnO2 and Fe 2O3, CoO, NiO, CuO, ZnO and SrO, Y2O3, ZrO2 system, etc. are mentioned, for example.

[0042] Although the particle can also be independently used for the metallic oxide mentioned above as a carrier core, it is desirable to process to oxidize a core front face intensely in that case etc., to carry out specific resistance of a carrier core more than 1x1010-ohmcm, and to use it. Moreover, in this invention, as a form of a desirable carrier core, into a binder resin, the metallic oxide (ferromagnetic) which has at least one sort of magnetism out of a metallic oxide which was described above is distributed, a carrier core particle is formed, and it uses as a distributed magnetism carrier especially. In this case, although one kind of metallic oxide can also be distributed and used into a binder resin, preferably, it uses, where at least two or more sorts of metallic oxides are mixed, and these are distributed in a binder resin, and a carrier core particle is formed especially. Especially in this invention, it is desirable to use at least one of the metallic oxides as a ferromagnetic, and to make at least one into other metallic oxides of high resistance rather than this ferromagnetic.

[0043] Moreover, in this invention, it is desirable that the front face of the metallic oxide used with the resin carrier core (it is also hereafter called a metallic-oxide distribution resin core) which distributed the metallic oxide in the binder resin is lipophilic--ization-processed. That is, if the lipophilic--ization-processed metallic oxide is distributed in a binder resin and a carrier core particle is formed, this metallic oxide will become possible [being incorporated in a binder resin uniformly and with high density]. In forming a carrier core particle by the polymerization method especially, in order to obtain a particle with a smooth front face in a globular form, and in order to make particle size distribution sharp, it is important to use this lipophilic--ization-processed metallic oxide.

[0044] In this case, the method of making a front face lipophilic is mentioned by distributing a metallic oxide in the aquosity solvent which processes a metallic oxide by the silane system coupling agent and coupling agents, such as a titanate system coupling agent, or contains a surfactant as the method of the lipophilic-ized processing performed. As a silane system coupling agent here, what has a hydrophobic radical, an amino group, or an epoxy group can be used. As a silane system coupling agent which has a hydrophobic radical, vinyl trichlorosilan, vinyltriethoxysilane, a vinyl tris (beta-methoxy) silane, etc. can be mentioned, for example. As a silane system coupling agent which has an amino group, gammaaminopropyl ethoxy silane, N-beta (aminoethyl)-gamma-aminopropyl trimethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl MEECHIRU dimethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, etc. are mentioned, for example. As a silane system coupling agent which has an epoxy group, gamma-glycidoxypropylmethyldietoxysilane, gamma-glycidoxy propyltriethoxysilane, beta-(3, 4-epoxy SHIKUKURO hexyl) trimethoxysilane, etc. are mentioned, for example. [0045] As a titanate system coupling agent, isopropylisostearoyl titanate, isopropyl tridodecyl benzenesulphonyl titanate, isopropanal pel tris (dioctyl pyrophosphate) titanate, etc. can be mentioned, for example. Moreover, as a surfactant used in this case, various kinds of commercial surfactants can be used as they are.

[0046] In this invention, when using two or more sorts of metallic oxides for formation of a carrier core particle, it is more desirable to use the particles of the metallic oxide to which specific gravity and the configuration are similar, when raising the improvement in adhesion and carrier intensity with a binder resin. For example, as such a combination, a magnetite, a hematite and a magnetite, a maghemite (gamma-Fe 2O3) and a magnetite, SiO2 and a magnetite, aluminum 2O3 and a magnetite, TiO2 and a magnetite, a Cu-Zn system ferrite, etc. can be mentioned. Also in this, the combination of a magnetite and a hematite is desirable especially from a price side and the on-the-strength side as a toner particle. [0047] Furthermore, in this invention, although the number mean particle diameter of the metallic oxide which shows the magnetism used in this invention changes also with carrier particle size, the thing to 0.02 or 2 micrometers is used preferably. Moreover, when making it distribute in a binder resin and using these using two or more sorts of above-mentioned metallic oxides, as a metallic oxide which has ferromagnetism, it is desirable that a number mean particle diameter uses the thing to 0.02 or 2 micrometers, and it is desirable to use 0.05 or a 5-micrometer thing as a number mean particle diameter of the metallic oxide of high resistance rather than this ferromagnetic of another side. In this case, it is

desirable that particle-size ratio rb/ra with the particle size (rb) of the metallic oxide of high resistance exceeds 1.0 rather than another of this ferromagnetic to the particle size (ra) of a ferromagnetic particle preferably especially. Furthermore, it is desirable preferably that the value of particle-size ratio rb/ra is 1.0 or 5.0. That is, it becomes easy to come to a front face out of the metallic-oxide particle which is it the low ferromagnetic of specific resistance with a big particle size that the value of rb is smaller than the value of ra, and is less than 1.0 times, and the prevention effect of the carrier adhesion which this invention makes the purpose so that it may become impossible to fully raise the specific resistance of a carrier core particle and it may be mentioned later becomes is hard to be acquired. Moreover, if the value of rb exceeds 5.0 times of the value of ra, since incorporation of the metallic-oxide particle to the inside of a binder resin will stop succeeding, the intensity of a magnetic carrier will fall and it will become easy to cause carrier destruction, it is not so desirable. In addition, about the particle-size measuring method of the metallic oxide used by this invention, it mentions later. [0048] When distributing a metallic oxide and producing a carrier core particle in a binder resin, as a metallic-oxide particle which has magnetism, it is desirable to use the thing of 1x103 or more ohm-cm as specific resistance of the metallic oxide to be used. It is not desirable, in order desired carrier specific resistance is not obtained though the quantity of the content of the metallic-oxide particle distributed as the specific resistance of a metallic-oxide particle which has magnetism is less than 1x103 ohm-cm is decreased, but to cause charge pouring, to lower quality of image or to cause carrier adhesion. As point \*\* was carried out especially in this case, when mixing and using two or more sorts of metallic oxides, it is desirable for specific resistance to use the thingohm [1x103] and more than cm, and to use what has specific resistance higher than this as a metallic-oxide particle of another side different from this for the metallic-oxide particle which is a ferromagnetic. In this case, as specific resistance of the metallic oxide of another side to be used, the thing of 1x108 or more ohm-cm is used preferably. In using the carrier core particle which distributed two or more sorts of metallic oxides in the resin here As stated previously, as a metallic-oxide particle of another side Although it is desirable to make a metallic oxide with a big particle size contain, to be easy to come to the front face of a carrier core particle out of this metallic-oxide particle, and to make it consist of a metallic-oxide particle which is a ferromagnetic, if the specific resistance of this metallic oxide is less than 1x108 ohm-cm Specific resistance of the carrier core particle formed cannot fully be raised, but it is a book. In addition, about the specific resistance measuring method of the metallic oxide used by this invention, it mentions later. [0049] Moreover, when using a metallic-oxide distribution resin core on the magnetic carrier which constitutes the binary system developer of this invention, it is desirable to use what contains 50 % of the weight or 99% of the weight of a metallic oxide in a core. Since electrification nature becomes it unstable that the content of a metallic oxide is less than 50 % of the weight, a carrier is charged especially under low-humidity/temperature environment, the residual charge becomes easy to remain and a fines toner, an external additive, etc. become easy to adhere to a carrier front face, it is not desirable. On the other hand, if the content of a metallic oxide exceeds 99 % of the weight, carrier intensity will fall, and it becomes easy to produce problems, such as a crack of the carrier by durability. [0050] Furthermore, it is desirable that the content of the metallic oxide which has the magnetism occupied to the whole metallic oxide which contains two or more sorts of metallic oxides in the metallic-oxide distribution resin core distributed in the binder resin as a desirable form of this invention is 30 % of the weight or 95 % of the weight. Although high resistance-ization of a core becomes it good that the amount of the metallic oxide which has magnetism is less than 30 % of the weight, the magnetic force as one side and a magnetic carrier becomes small, and the case where carrier adhesion is caused arises. On the other hand, if it exceeds 95 % of the weight, although it will be based also on the specific resistance of the metallic oxide which has magnetism, high resistance-ization of a more desirable core cannot be achieved.

[0051] All the resins obtained by carrying out the polymerization of the vinyl system monomer as a binder resin used for the above-mentioned metallic-oxide distribution resin core used by this invention can be mentioned. As a vinyl system monomer said here, for example Styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, p-phenyl styrene, p-ethyl styrene, 2, 4-dimethyl styrene, p-n-butyl

styrene, p-tert-butyl styrene, p-n-hexyl styrene, p-n-octyl styrene, p-n-nonyl styrene, p-n-desyl styrene, p-n-dodecyl styrene, Styrene derivatives, such as p-methoxy styrene, p-crawl styrene, 3, 4-dichloro styrene, m-nitroglycerine styrene, o-nitroglycerine styrene, and p-nitroglycerine styrene, Ethylene and unsaturation monoolefins, such as ethylene, a propylene, a butylene, and an isobutylene; A butadiene, Unsaturation diolefins, such as an isoprene, a vinyl chloride, a vinylidene chloride, Halogenation vinyls, such as vinyl bromide and a fluoride vinyl; Vinyl acetate, a propionic-acid vinyl, Vinyl esters, such as a BENZOE acid vinyl; A methacrylic acid and a methyl methacrylate, An ethyl methacrylate, a methacrylic-acid propyl, methacrylic-acid n-butyl, A methacrylic-acid isobutyl, a methacrylic-acid noctyl, a methacrylic-acid dodecyl, alpha-methylene aliphatic monocarboxylic-acid ester, such as methacrylic-acid-2-ethylhexyl, stearyl methacrylate, and a methacrylic-acid phenyl; An acrylic acid and a methyl acrylate, An ethyl acrylate, acrylic-acid n-butyl, isobutyl acrylate, An acrylic-acid propyl, an acrylic-acid n-octyl, an acrylic-acid dodecyl, Acrylic-acid 2-ethylhexyl, acrylic-acid stearyl, acrylic-acid 2-crawl ethyl, Acrylic esters, such as an acrylic-acid phenyl; A MAREN acid, a maleic-acid half ester; vinyl methyl ether, Vinyl ether, such as vinyl ethyl ether and the vinyl isobutyl ether; A vinyl methyl ketone, Vinyl ketones, such as a vinyl hexyl ketone and a methyl isopropenyl ketone N-vinyl pyrrole, Nvinylcarbazole, N-vinyl indole, N-vinyl compound [, such as N vinylpyrrolidone, ]; -- vinyl naphthalene; -- acrylonitrile -- An acrylic acid or methacrylic-acid derivatives, such as a methacrylonitrile and an acrylamide; acroleins are mentioned and one sort or the thing which used two or more sorts and carried out the polymerization is used out of these.

[0052] Moreover, the mixture of non-vinyl condensed-system resins, such as polyester resin, an epoxy resin, phenol resin, a urea-resin, a polyurethane resin, polyimide resin, a cellulosic resin, and a polyether resin, or the these and the aforementioned vinyl system resin can be used in addition to the resin obtained from a vinyl system monomer by carrying out a polymerization.

[0053] After fully mixing additives, such as the above-mentioned thermoplastics of a vinyl system and a non-vinyl system and a metallic oxide, and other curing agents, with a mixer as a method of manufacturing the metallic-oxide distribution resin core used by this invention, using kneading machines, such as a heating roller, a kneader, and an extruder, it kneads and melting and the method of grinding, performing a classification after cooling this, and obtaining a carrier core are mentioned. In this invention, it is desirable heat or to globular-form-ize mechanically and to use as a core the metallic-oxide content resin particle obtained as mentioned above on this occasion.

[0054] Moreover, there are also mixture and a method of carrying out a polymerization and obtaining a carrier core about the direct, for example, vinyl mentioned above, system monomer and metallic oxide other than a method which carry out melting kneading, grind the above-mentioned binder resin and the metallic oxide mentioned above as a method of manufacturing the metallic-oxide distribution resin core used by this invention, and are used as a carrier core. At this time, bisphenols, the phenols of epichlorohydrin and phenol resin, aldehydes, the urea of a urea-resin and aldehydes, the melamine and aldehydes etc. it is incomparable in the start raw material of an epoxy resin other than a vinyl system monomer are used as a monomer used for a polymerization. For example, in an aquosity medium, the metallic oxide and distributed stabilizer which were mentioned above under existence of a basic catalyst are put in using phenols and aldehydes as the manufacture method of the metallic-oxide distribution resin core using hardening system phenol resin, a suspension polymerization is carried out, and a core is obtained.

[0055] It is desirable to make a binder resin which was raised above construct a bridge, and to use it, in order to make the intensity of a metallic-oxide distribution resin particle raise as a method of manufacturing the especially desirable metallic-oxide distribution resin core used in this invention or for the coat of the resin to be made to be carried out to fitness on a metallic-oxide distribution resin particle more further. And the method of using the method of choosing the method of adding a bridge formation component and making it construct a bridge at the time of kneading or the hardened type resin hardened according to bridge formation as a binder resin, when carrying out melting kneading of a resin and the metallic oxide, using with a metallic oxide, carrying out direct polymerization, and obtaining a core as a method of making a binder resin constructing a bridge, for example, or the monomer which put in the

bridge formation component can be mentioned.

[0056] Furthermore, in this invention, it is desirable that the front face of a carrier core particle which consists of a metallic-oxide distribution resin particle which was described above is covered with the suitable coat resin chosen according to the amount of electrifications of the toner used with a carrier in this invention. In such a coat magnetism carrier, as for the amount of coat resins on the front face of a core covered with the resin, it is desirable that it is 0.1 % of the weight or 10% of the weight of a range, and it is still more suitable for it that it is 0.3 % of the weight or 5% of the weight of a range. Moreover, when the metallic-oxide distribution resin particle front face used by this invention described previously considers as within the limits which described the amount of coats of a resin above in the coat magnetism carrier covered with the coat resin, it is more desirable in order for it to prevent carrier adhesion that the average exposure density of the metallic oxide of the front face of a coat magnetism carrier carries out to two or less [5 //micrometer] good. Furthermore, it carries out to two or less [3 //micrometer] preferably.

[0057] It becomes difficult for the amount of coat resins by the above-mentioned coat resin to fully carry out the coat of the carrier core particle front face at less than 0.1 % of the weight, especially sufficient electrification grant control to a toner becomes difficult after durability. moreover -- although it can consider as the range of a request of the specific resistance of a magnetic carrier since there are too many amounts of coat resins, if it exceeds 10 % of the weight -- that a fluidity falls \*\*\*\* -- many -- it is not desirable in respect of the durable picture property by the copy of several sheets deteriorating etc. In addition, the calculation method of the average exposure density of the metallic oxide of a coat magnetism carrier front face is mentioned later.

[0058] As a coat resin for covering the carrier core front face which can be used in this invention, an insulating resin can be used suitably. You may be thermosetting resin even if it is thermoplastics as an insulating resin used here. in this case, as a thermoplastic resin which can be used Specifically For example, acrylic resin, such as polystyrene, a polymethylmethacrylate, and a styrene-acrylic-acid copolymer, A styrene-butadiene copolymer, an ethylene-acid vinyl copolymer, a vinyl chloride, Vinyl acetate, a polyvinylidene-fluoride resin, a fluorocarbon resin, a perphloro carbon resin, A solvent fusibility perphloro carbon resin, polyvinyl alcohol, a polyvinyl acetal, A polyvinyl pyrrolidone, a petroleum resin, a cellulose, cellulose acetate, a cellulose nitrate, A methyl cellulose, a hydroxymethyl cellulose, a hydroxyethyl cellulose, Cellulosics, such as hydroxypropylcellulose, a novolak resin, Low molecular weight polyethylene, saturation alkyl polyester resin, a polyethylene terephthalate, The aromatic-polyester resin called the polybutylene terephthalate and polyarylate, Polyamide resin, polyacetal resin, polycarbonate resin, a polyether sulphone resin, polysulfone resin, polyphenylene sulfide resin, and polyether ketone resin can be mentioned.

[0059] As a hardenability resin, specifically Moreover, phenol resin, denaturation phenol resin, A mallein resin, alkyd resin, an epoxy resin, acrylic resin For example, the unsaturated polyester obtained according to the polycondensation of maleic-anhydride-terephthalic-acid-polyhydric alcohol, A urearesin, melamine resin, urea-melamine resin, a xylene resin, a toluene resin, A guanamine resin, a melamine-guanamine resin, an acetoguanamine resin, glyptal resin, a furan resin, silicone resin, a polyimide, a polyamidoimide resin, polyetherimide resin, a polyurethane resin, etc. can be mentioned. Each may be mixed and used for it although the resin mentioned above can be used even if it is independent. Moreover, it can also be used, making the above-mentioned thermoplastics able to mix and harden a curing agent etc.

[0060] The spray of the coat resin solution which was described above while carrying out a suspension flow of the carrier core material formed of the binder resin described previously and a metallic oxide as the desirable manufacture method of the coat magnetism carrier used in this invention is carried out, and the method of making a coat film form in a core material front face, the spray-drying method, etc. are mentioned. When carrying out the coat especially of the above-mentioned coat method to the metallic-oxide distribution resin core which used thermoplastics as a coat resin, it is suitable. Although other coat methods of volatilizing a solvent gradually are mentioned as the other coat methods, applying shearing stress, the coat magnetism carrier used by this invention also by the method concerned can be

manufactured suitably. The method of hardening a coat and cracking etc. is mentioned applying the method of cracking the carrier made to specifically fix as this method after volatilizing a solvent above the glass transition point of a coat resin, and shearing stress.

[0061] As for the bulk density of the magnetic carrier which constitutes the binary system developer of this invention obtained as mentioned above, it is desirable that it is three or less 3.0 g/cm. If 3.0 g/cm<sup>3</sup> are exceeded, since the share in the inside of a developer will become large too much and will become easy to produce SUPENTO to the toner of coat material, or coat peeling, it is not desirable. In addition, it sets to this invention and measurement of the bulk density of a carrier is IIS. According to the method of a publication, it carries out to K5101. Furthermore, as a configuration of the magnetic carrier used in this invention, you may be what thing, and the carrier of a configuration which is convenient for a predetermined system can be chosen and used suitably. However, in this invention, it is desirable to have a configuration near the globular form whose degree-of-sphericity SF-1 of a carrier is 200 or less. That is, if degree-of-sphericity SF-1 of the magnetic carrier used in this invention exceeds 200, it will become an indeterminate form, and the fluidity as a developer comes to be inferior in the binary system developer with which this carrier is constituted by containing, phenomena, like on the fall of the triboelectrification grant capacity to a toner and a development pole, the configuration of a magnetic brush becomes uneven arise, and a high definition picture becomes is hard to be acquired. [0062] In this invention, the degree of sphericity of a carrier extracts 300 or more carriers at random with the scanning electron microscope S-4500 by Hitachi [, Ltd. ], Ltd., measures, and is performed by asking for the degree of sphericity drawn by the following formula using the image-processing analysis equipment Luzex3 made from NIREKO. Here, the degree of sphericity means that it is so close to a sphere that it is close to 100.

a degree of sphericity -- SF-1={(MX LNG)2-/AREA} xpi / 4x100[-- MX LNG is the overall diameter of a carrier among the above-mentioned formula, and AREA expresses the projected area of a carrier] [0063] Next, the composition of the toner used for the binary system developer of this invention is explained. The toner used for this invention contains the binding resin 100 weight section, a coloring agent 0.1, or 15 weight sections. A number mean particle diameter is 0.5 or 10.0 micrometers. the number distribution accumulation value below the diameter of 1-/double precision of a number mean particle diameter (D1) Several 10% or less, The volume-integral cloth accumulation value more than the diameter of double precision of a volume mean particle diameter (D3) is below 10 volume %, and it is desirable that the coefficient of variation of the particle size distribution of number criteria is 20% or less in order to satisfy the repeatability of the good electrification grant without a reversal component, and a latent-image dot.

[0064] furthermore, in order to make electrification nature of a toner good and to raise dot repeatability As for the toner used by this invention, it is desirable that a number mean particle diameter is in 1.0 or the range of 6.0 micrometers. It is 3.0 or 6.0 micrometers more preferably, the number distribution accumulation value below the diameter of 1-/double precision of the number mean particle diameter (D1) of a toner It is several 2% or less more preferably several 5% or less, the volume-integral cloth accumulation value more than the diameter of double precision of a volume mean particle diameter (D3) Below 5 volume %, it is below 2 volume % still more preferably, and it is preferably desirable that the coefficient of variation of the particle size distribution of number criteria is 10% or less more preferably 15% or less.

[0065] that is, since the particle diameter of the piece which develops an electrostatic latent image becomes large when the number mean particle diameter of the toner used by this invention exceeds 10.0 micrometers, though the magnetic force of a carrier is lowered how much, development faithful to a latent image carries out -- having -- hard -- further -- a static -- since it becomes easy to produce spilling of a toner when performing a \*\*\*\* imprint, it is not desirable On the other hand, if the number mean particle diameter of a toner is set to less than 0.5 micrometers, it will be easy to produce un-arranging to the handling nature as fine particles.

[0066] moreover, when the number distribution accumulation value of the small toner particle below the diameter of 1-/double precision of the number mean particle diameter (D1) of a toner exceeds several

10% It will not be able to carry out good, but the TORIBO distribution of a toner will spread, and the mean particle diameter of the toner in the development counter in durability and change of particle size distribution will produce the triboelectrification grant to a fines toner particle by poor electrification (generation of the reversal component charged in reversed polarity), and developed maldistributionization of the grain size of a toner.

[0067] On the other hand, when the volume-integral cloth accumulation value of the big toner particle more than the diameter of double precision of the volume mean particle diameter (D3) of a toner exceeds 10 volume %, it becomes difficult to be unable to perform triboelectrification with a carrier good, and to resemble a bird clapper, in addition to reproduce an electrostatic latent image faithfully. [0068] Furthermore, when it is the thing of high resolution [ as / whose electrostatic latent image is 600 or more dpi especially when the coefficient of variation of the particle size distribution of the number criteria of a toner exceeds 20%], the repeatability of a dot falls. In addition, about the method of measuring the particle size distribution of a toner, it mentions later.

[0069] Moreover, in this invention, the globular form toner whose shape factor SF-1 is 100 or 140 is used. Furthermore, the thing of 100 or 130 is preferably used for SF-1 suitably. Here, SF-1 which shows the shape factor used by this invention samples 100 toner images at random, it analyzes by introducing the image information into the image-analysis equipment made from NIREKO (Luzex3) through an interface using Hitachi FE-SEM (S-4500), and is defined by the value computed and acquired from the lower formula.

[0070] a shape factor -- SF-1={(MXLNG)2-/AREA} xpi / 4x100[-- MXLNG is the overall diameter of a toner among the above-mentioned formula, and AREA is the projected area of a toner] As shown in the above-mentioned formula, shape factor SF-1 of a toner shows the globular form degree of a toner, and if SF-1 is larger than 140, it will become an indeterminate form from a globular form gradually.

[0071] Furthermore, it is a book when a part or the whole uses the toner formed by the polymerization method in the binary system developer of this invention as a toner which constitutes this developer. Especially the toner that formed the surface portion of a toner by the polymerization method is made to exist as a pre toner (monomer constituent) particle in a dispersion medium, and in order to carry out the polymerization of the required portion by polymerization reaction and to produce it, it has the front-face nature by which smoothing was carried out considerably. The operation effect of smoothing on the front face of a toner in this invention is collected by that electric field tend to concentrate on the so-called sharp portion of a toner. That is, since there is no place which a corona shower or electric discharge concentrates on a part for heights, and a corona shower or electric discharge will concentrate to the portion having the property of deteriorating specifically if the toner front face is smooth when the toner which passed through photo conductor electrification process is the existing so-called uneven toner, it is thought that it is hard to cause toner degradation. If the value of toner configuration SF-1 becomes an indeterminate form exceeding 140, picture fogging may increase or endurance may be inferior a little. [0072] Furthermore, it is desirable to use the outside \*\* toner with which the external additive is added by the toner particle front face as a toner used in this invention. That is, the fluidity of a developer improves in an external additive existing in the effect, the toner and the carrier, or between toners by using the outside \*\* toner by which the toner particle front face is covered with the external additive. [ which misses the influence on the toner by the photo conductor live-part material described previously to a certain partial external additive ] Furthermore, although it is desirable to make improvement in the life of a developer, in this invention from the meaning, it is desirable 5 or to make still more preferably the external additive coverage of a toner particle front face into 10 or 99% 99%.

[0073] As an external additive added by the toner, an aluminum oxide, titanium oxide, A strontium titanate, a cerium oxide, a magnesium oxide, a chrome oxide, Carbide [, such as nitride; silicon carbide ], such as metallic oxides, such as a tin oxide and a zinc oxide, and silicon nitride; A calcium sulfate, Fatty-acid metal salts, such as metal salt; zinc stearates, such as a barium sulfate and a calcium carbonate, and a calcium stearate; in addition to this It is suitable to add the impalpable powder called carbon black, a silica, polytetrafluoroethylene, polyvinylidene fluoride, a polymethylmethacrylate,

polystyrene, and silicone. Moreover, as for the number mean particle diameter of the impalpable powder of an external additive which was mentioned above, it is desirable that it is 0.1 micrometers or less. If the number mean particle diameter of an external additive exceeds 0.1 micrometers, the effect of fluid improvement may be lost, a toner development, the defect at the time of an imprint, etc. may be produced, quality of image may be reduced, and it is not desirable.

[0074] Moreover, for an external additive which is \*\*(ed) by the toner outside in this invention and which was described above, it is 0.05 or 5 weight \*\*\*\*\*\*\*\* that 0.01 or 10 weight sections are used to the toner particle 100 weight section desirable still more preferably. Even if it uses independently, you may use together two or more above-mentioned external additives. Furthermore, it is more desirable to use that by which hydrophobing processing was performed to each. In addition, in this invention, 100 toner images were sampled for the external additive coverage on the front face of a toner at random using Hitachi FE-SEM (S-800), and it analyzed by having introduced into the image-analysis equipment made from NIREKO (Luzex3) through the interface, the image information was computed, and it asked for it.

[0075] Moreover, as a surface area of the external additive impalpable powder used for this invention, the thing of the range of 50 or 600m2/g has an especially good specific surface area by the nitrogen adsorption by the BET adsorption method more than 30m2/g. Moreover, \*\*\*\*\* can be performed outside the toner and external additive which consist of such an impalpable powder using mixers, such as a Henschel mixer.

[0076] this invention -- setting -- the above -- it mixes with the magnetic carrier particle described previously, and let the toner obtained by making it like be the binary system developer of this invention Although it is dependent also on the development process to apply when forming a binary system developer, typically, it is suitable 1 or that the rate of the toner in a developer considers as 1 or 10% of the weight of the range more preferably 20% of the weight. Moreover, it is suitable for the binary system developer of this invention that the amount of triboelectrification is in the range of 5 or 100microC/g, and it should just be in the range of 5 or 60microC/g most preferably. In addition, about the measurement conditions of the amount of triboelectrification used by this invention, it mentions later. [0077] As a monomer of the polymerization nature used for the binding resin of a toner used for this invention, if it is the monomer of radical polymerization nature, all polymerization nature monomers can be used. Specifically For example, styrene, o-methyl styrene, m-methyl styrene, Styrene system monomers, such as p-methoxy styrene, p-ethyl styrene, and p-tertiarybutyl styrene, An acrylic acid, a methyl acrylate, an ethyl acrylate, acrylic-acid n-butyl, An acrylic-acid n-propyl, isobutyl acrylate, an acrylic-acid octyl, An acrylic-acid dodecyl, acrylic-acid 2-ethylhexyl, acrylic-acid stearyl, Acrylic esters, such as acrylic-acid 2-crawl ethyl and an acrylic-acid phenyl A methacrylic acid, a methyl methacrylate, an ethyl methacrylate, a methacrylic-acid n-propyl, Methacrylic-acid n-butyl, a methacrylic-acid isobutyl, a methacrylic-acid n-octyl, A methacrylic-acid dodecyl, methacrylic-acid 2ethylhexyl, stearyl methacrylate, A methacrylic-acid phenyl, methacrylic-acid dimethyl aminomethyl, a methacrylic-acid diethylaminoethyl, Methacrylic esters, such as a methacrylic-acid benzyl, 2hydroxyethyl acrylate, On a vinyl derivative besides being acrylonitrile besides 2-hydroxyethyl meta-KUREREITO, methacrylic nitril, an acrylamide, etc., and a concrete target For example, the methyl vinyl ether, ethyl vinyl ether, propyl vinyl ether, Alkyl vinyl ether, such as n-butyl ether and the isobutyl ether beta-crawl ethyl vinyl ether, phenyl vinyl ether, p-methylphenyl ether, Diene compounds, such as p-crawl phenyl ether, p-bromine phenyl ether, p-nitrophenyl vinyl ether, p-methoxypheny vinyl ether, and a butadiene, can be mentioned. Preferably, these polymerization nature monomers are good in their being a liquid or a solid-state under ordinary temperature and an ordinary pressure. [0078] Moreover, these monomers can choose independent or suitable polymer composition from which

[0078] Moreover, these monomers can choose independent or suitable polymer composition from which it can be used, mixing and a desirable property is acquired. In the toner used by this invention, a melt viscosity property can be adjusted if needed by making the amount component of macromolecules, or a gel component contain. Introduction of such a component is attained by using the cross linking agent which has two or more double combination per monad of polymerization nature. As this cross linking agent, specifically For example, aromatic divinyl compounds, such as a divinylbenzene and divinyl

naphthalene, Ethylene glycol diacrylate, ethylene glycol dimethacrylate, Triethylene-glycol dimethacrylate, tetraethylene-glycol dimethacrylate, 1, 3-butylene-glycol dimethacrylate, trimethylolpropane triacrylate, Trimethylolpropanetrimethacrylate, 1, 4-butanediol diacrylate, Neopentyl glycol diacrylate, 1, 6-hexanediol diacrylate, A pentaerythritol thoria chestnut rate, pen TAERISURI rate tetraacrylate, Pentaerythritol dimethacrylate, pentaerythritol tetrapod methacrylate, Compounds, such as glycerol bitter taste ROKISHI dimethacrylate, N, and N-divinyl aniline, the divinyl ether, a divinyl sulfide, and a divinyl sulfone, can be mentioned, and you may use two or more kinds, mixing suitably. It can also mix beforehand into polymerization nature mixture, and this cross linking agent can also be suitably added in the middle of a polymerization if needed.

[0079] In case the toner of this invention is formed, moreover, an acrylic acid, a methacrylic acid, a crotonic acid, On an itaconic acid, a maleic acid, a fumaric acid, itaconic-acid monobutyl, maleic-acid monobutyl, a phosphoric-acid content monomer, and a concrete target Acid phosphoxyethyl metacrylate, acid phosphooxy propyl methacrylate, A sulfonic group content monomer, dimethylamino ethyl acrylate, diethylamino ethyl methacrylate, A bitter taste roil morpholine, 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, N vinylpyrrolidone, 2-vinyl imidazole, an N-methyl-2-vinyl imidazole, and N-vinyl imidazole -- or although mentioned above, salts etc. can be copolymerization-ized and electrification nature can also be adjusted

[0080] As a method of manufacturing the toner used by this invention Specifically JP,36-10231,B, a JP,59-53856,A official report number, The method of producing a direct toner using the suspensionpolymerization method stated to the JP,59-61842,A official report number, The distributed polymerization method which generates a direct toner using the insoluble drainage system organic solvent to the polymer which is meltable to a monomer and is obtained, or the emulsion-polymerization method represented by the soap free polymerization method which carries out direct polymerization under existence of a water-soluble polarity polymerization initiator, and generates a toner is mentioned. [0081] The particle size distribution especially used for this invention are sharp, and, as for the globular form toner with few contents of a low molecular weight constituent, obtaining by the following manufacture methods is desirable. Namely, although the polymerization nature monomer for compounding the binding resin of a toner is dissolved The organic solvent in which the binding resin obtained by compounding a polymerization nature monomer is not dissolved, Or in the solvent like the mixed solvent which has such an organic solvent and water, dissolve the high molecular compound and/or surfactant as matrix polymer, and a solution is prepared. The way carry out the polymerization of the polymerization nature monomer under existence of a polymerization initiator in the system of reaction which dissolved the above-mentioned polymerization nature monomer at least into this solution under nitrogen atmosphere, and this obtains a toner particle is good. As a high molecular compound dissolved into this solvent, you may use two or more sorts together. Furthermore, an electric charge control agent and a coloring agent can be dissolved or distributed in the system of reaction, a polymerization can be performed, and this \*\*\*\*\* agent and coloring agent can also be made to contain in a toner particle at the time of the polymerization of the polymerization nature monomer in the inside of the system of reaction.

[0082] That in which the binding resin of a toner deposits with advance of a polymerization as an organic solvent used when compounding a toner particle by the above-mentioned polymerization method is mentioned. Specifically For example, a methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutyl alcohol, Tertiary butyl alcohol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-BUTANJI Norian, isopentyl alcohol, Tertiary pentyl alcohol, 1-hexanol, a 2-methyl-1-pentanol, A 4-methyl-2-pentanol, 2-ethyl butanol, 1-heptanol, The fatty alcohol of the straight chain like 2-heptanol, 3-heptanol, 2-octanol, and a 2-ethyl-1-hexanol, or a branched chain; A pentane, 2-methyl butane, n-hexane, a cyclohexane, 2-methyl pentane, 2 and 2-dimethyl butane, 2, 3-dimethyl butane, a heptane, n-octane, An isooctane, 2 and 2, a 3-trimethyl pentane, Deccan, a nonane, A cyclopentane, a methylcyclohexane, a methylcyclohexane, ethylcyclohexane, p-menthonaphtene and the aliphatic hydrocarbon; aromatic carbonization water; halogenated hydrocarbons like a bicyclo hexyl; ether; fatty-acids; ester; sulphur-containing compound; and those mixture can be mentioned. Moreover, these matter

can also be mixed and used.

[0083] Moreover, as a high molecular compound used by the above-mentioned polymerization method, these organic solvents used in the case of a polymerization or the thing to dissolve in the mixed solution of these and water can be used. Specifically For example, polystyrene, a polymethylmethacrylate, a phenol novolak resin, A cresol novolak resin, a styrene-acrylic copolymer, the polymethyl vinyl ether, Vinyl ether copolymers, such as poly ethyl vinyl ether, the poly butyl vinyl ether, and the poly isobutyl vinyl ether, Polyvinyl alcohol, polyvinyl acetate, a styrene-butadiene copolymer, An ethylene vinylacetate copolymer, a polyvinyl pyrrolidone, polyhydroxy styrene, A vinyl chloride, a polyvinyl acetal, a cellulose, cellulose acetate, a cellulose nitrate, an alkylation cellulose, a hydroxyalkyl-ized cellulose), such as a hydroxymethyl cellulose and hydroxypropylcellulose, saturation alkyl polyester resin, an aromatic-polyester resin, polyamide resin, a polyacetal, polycarbonate resin or these copolymers, mixture, etc. can be mentioned to (concrete target.

[0084] the organic solvent or mixed solvent described above as amount of these high molecular compounds used in the above-mentioned polymerization method -- receiving -- 0.1 % of the weight -- or it is preferably good 0.5 % of the weight or 1% of the weight of that it is 20 % of the weight still more preferably 30% of the weight 50% of the weight It can mix with the distributed stabilizer of independent or others, and a high molecular compound and/or a copolymer can be used. In case a particle toner is formed by the above-mentioned method, a particle generates with advance of a reaction. Although the obtained particle is repeatedly washed by a reaction solvent or other suitable solvents, in order to improve washing efficiency, it can also use separation meanses, such as a centrifugal separator, in that case. By drying and cracking the obtained toner a \*\* exception after washing, a particle is obtained, a predetermined additive can be added suitably and the toner of this invention can be obtained. Under the present circumstances, atomizing processes, such as spray dry, can also be used as separation and a dryness means.

[0085] Anything that is known as a radical initiator can be used as a polymerization initiator used in the above-mentioned polymerization method. As this polymerization initiator, for example 2 and 2'-azobis (2,4-dimethylvaleronitrile), - azobisisobutyronitril, and 2 and 2'1, 1'-azobis - (cyclohexane-1-carbonitrile), An azo system or diazo series polymerization initiators, such as 2 and 2'-azobis-4-methoxy 2,4-dimethylvaleronitrile, - azobis (2-AMINOJI propane) dihydrochloride, and 2 and 2'2, 2'-azobis (N and N'-dimethylene isobutyl amidine), Amidine compounds, such as 2 and 2'-azobis (N and N'-dimethylene isobutyl amidine) dihydrochloride, Benzoyl peroxide, methyl ethyl ketone peroxide, diisopropyl par OKISAISHI carbonate, The mixture of peroxide system polymerization initiators, such as cumene hydronalium peroxide, 2, 4-dichlorobenzoyl peroxide, and lauroyl peroxide, and potassium persulfate, a persulfide system initiator called an ammonium persulfate, and the polymerization initiator further mentioned above can be mentioned.

[0086] moreover, the above-mentioned polymerization method -- setting -- a conventionally well-known chain transfer agent -- concrete -- a carbon tetrachloride, carbon tetrabromide, 2 ethyl bromoacetates, acidulous-smell-ized ethyl acetate, and 2 bromination -- ethylbenzene -- disulfide, such as mercaptans, such as hydrocarbons, such as halogenated hydrocarbons, such as ethane and 2 chlorination ethane, a diazo thioether, benzene, ethylbenzene, and an isopropylbenzene, a tertiary dodecyl mercaptan, and n-dodecyl mercaptan, and diisopropyl ZANTO gene disulfide, can also be added 2 bromination Although it can adjust suitably in consideration of the molecular weight of the polymer manufactured, yield, etc. as such polymerization initiator concentration used in case the toner used by this invention is obtained by the above-mentioned polymerization method, it is suitable to be able to use it in 0.1 to 15% of the weight of the range of the total amount of the polymerization nature monomer to be used, and to use it especially in 0.5 to 12% of the weight of the range.

[0087] As a coloring agent used for the component of the toner used by this invention On various kinds of organic coloring agent besides carbon black, and a concrete target, specifically for example C. The I direct red 1, the C.I basic red 1, the C.I. mordant red 30, the C.I. direct blue 1, the C.I. direct blue 2, the C.I. acid blue 15, the C.I. basic blue 3, C.I. basic blue 5, C. The color called I. mordant blue 7, the C.I. direct green 6, the C.I. basic green 4, and C.I. basic green 6, A cadmium yellow, mineral first yellow,

navel orange yellow, Naphthol yellow S, Hansa yellow G, the permanent yellow NCG, A Tartrazine lake, molybdenum orange G TR, a benzidine orange G Cadmium red 4R, Watchung-Red cadmium salt, brilliant-carmine 3B, The fast biotechnology red B, a Violet Lake, cobalt blue, An alkali-blue lake, a Victoria-blue lake, a Quinacridone, a rhodamine lake, A copper phthalocyanine blue, a fast sky blue, the pigment green B Pigments, such as a marker-light green lake and the final yellow green G, etc. are reached. C. I. solvent yellow 6, the C.I. solvent yellow 9, the C.I. solvent yellow 17, the C.I. solvent yellow 31, the C.I. solvent yellow 35, the C.I. solvent yellow 100, C.I. solvent yellow 102, C. I. solvent yellow 103, the C.I. solvent yellow 105, the C.I. solvent orange 2, the C.I. solvent orange 7, the C.I. solvent orange 13, the C.I. solvent orange 14, the C.I. solvent orange 66, C. I. solven tread 5, the C.I. solven tread 16, the C.I. solven tread 17, the C.I. solven tread 18, the C.I. solven tread 19, the C.I. solven tread 22, the C.I. solven tread 143, C. I. solven tread 145, the C.I. solven tread 146, the C.I. solven tread 149, the C.I. solven tread 150, the C.I. solven tread 151, the C.I. solven tread 157, the C.I. solven tread 158, C. I. solvent biotechnology red 31, the C.I. solvent biotechnology red 32, the C.I. solvent biotechnology red 33, the C.I. solvent biotechnology red 37, the C.I. solvent blue 22, the C.I. solvent blue 63, C.I. solvent blue 78, C. I. solvent blue 83, the C.I. solvent blue 84, the C.I. solvent blue 85, the C.I. solvent blue 86, the C.I. solvent blue 104, the C.I. solvent blue 191, C.I. solvent blue 194, C. The color of I. solvent blue 195, the C.I. solvent green 24, the C.I. solvent green 25, C.I. solvent Brown 3, and C.I. solvent Brown 9 grade is desirable.

[0088] As a commercial color contained above, Mitsubishi Kasei G [ for example, / Diaresin; Yellow-3], Yellow-F, Yellow-H2G, Yellow-HG, Yellow-HC, Yellow-HL, Orange-HS, Orange-G, Red-GG, Red-S, Red-HS, Red-A, Red-K, Red-H5B, Violet-D, Blue-J, Blue-G, Blue-N, Blue-K, Blue-P, Blue-H3G, Blue-4G, Green-C, Brown-A, Indigo-dyeing SOT color [ made from the Hodogaya chemistry ]; Yellow-1, Yellow-3, Yellow-4, Orange-1, Orange-2, Orange-3, Scarlet-1, Red-1, Red-2, Red-3, Brown-2, Blue-1, Blue-2, Violet-1, Green-1, Green-2, Green-3, Black-1, Black-4, Black-6, and Black-8, The sudan color of BASF; Yellow-146, Yellow-150, Orange-220, Red-290, Red-380, Red-460, and Blue-670, The oil black made from the Orient chemical industry, oil-color; Yellow-3G, Yellow-GG-S, Yellow-#105, Orange-PS, Orange-PR, Orange-#201, Scarlet-#308, Red-5B, Brown-GR, Brown-#416, Green-BG, Green-#502, Blue-BOS, Blue-IIN, Black-HBB, Black-#803, Black-EB, Black-EX, the Sumitomo Chemical SUMIPU last; Blue GP, Blue OR Red-FB, red - 3B, yellow floor line7G, Yellow GC, and Nippon Kayaku make KAYARON Polyester Black EX-SF300, the kaya set RedB, blue A-2R, etc. can be mentioned.

[0089] Moreover, by this invention, a magnetic toner can also be further obtained as a coloring agent using the magnetic substance. Polymerization nature mixture can also be distributed beforehand, and after this coloring agent compounds only a macromolecule particle, into the solution which dissolves or distributed the required component, the aforementioned particle can be distributed, and it can be made to be able to color and also let it be a toner.

[0090] The polymerization toner formed using an above-mentioned method and an above-mentioned polymer can make various additives contain, in order to give a still more suitable developer property. It can also be made to mix and dissolve in polymerization nature mixture beforehand, and after these various additives compound a particle, they can also be added. An electric charge control agent can be added in order to control the electrification nature of the toner of this invention. Although it can use even if it is which thing of a right electric charge control agent or a negative electric charge control agent as an electric charge control agent, a metaphor can specifically mention a humic acid, salts, etc. which have the metallic compounds of a Nigrosine system color, a triphenylmethane-color system color, quarternary ammonium salt, an amine system or an imine system compound and a polymer, a salicylic acid, or an alkyl salicylic acid, an alloy monoazo color, a carboxylic acid, or a sulfonic-acid functional group, such as a polymer and a nitro humin.

[0091] Moreover, the toner used in this invention has 1 or a 10-micrometer number mean particle diameter, the distribution accumulation value of the particle more than ten-piece the diameter of double precision of several % or less and a volume mean particle diameter (D3) may classify [ the particle size distribution ] it, although the distribution accumulation value of the particle below the diameter of 1-

/double precision of a number mean particle diameter (D1) is below 10 volume %, and it may control particle size distribution. The hyperfractionation classifier using the inertia force is preferably used for the control method of particle size distribution. By using this equipment, the toner which has the abovementioned particle size distribution can be manufactured efficiently.

[0092] Development is carried out to the development method of this invention using the binary system developer which has composition which was described above using a development counter as shown in drawing 1. Specifically, it is desirable that a developer brush develops negatives by the latent-image support, for example, the state of being in contact with the photo conductor drum 3, impressing an alternating electric field to the developer support 1 (development sleeve). It is good in improvement in carrier antisticking and dot repeatability that the distance (distance between S-D) B of the development sleeve 1 and the photo conductor drum 3 is 100 or 1,000 micrometers. If the distance B between S-D is narrower than 100 micrometers, supply of a developer becomes inadequate, picture concentration stops coming out, and it is not desirable. Development pole S1 which is the magnetic field generating means by which the endocyst is carried out to the developer support inside of the body on the other hand if the distance B between S-D exceeds 1,000 micrometers The line of magnetic force of a shell spreads, the density of a magnetic brush becomes low, it is inferior to dot repeatability, or the force which restrains a carrier becomes weaker and carrier adhesion is produced.

[0093] moreover, the voltage between the peaks of an alternating electric field of the alternating electric field impressed to the development sleeve 1 in the development method of this invention is 500 or 5,000V -- desirable -- frequency -- 500 -- or 10,000Hz, it is 500 or 3,000Hz preferably, and these can be suitably chosen according to a process, respectively, and can be used Moreover, as a wave of the alternating electric field in this case, the wave which changed the triangular wave, the square wave, the sine wave, or the Duty ratio can be chosen variously, and it can use. Picture concentration with applied voltage as sufficient than 500V as a low is not obtained, and the fogging toners of the non-picture section may be unable to be collected good. On the other hand, when the voltage between the peaks of an alternating electric field exceeds 5,000V, through a development brush, a latent image may be disturbed on the contrary and a quality-of-image fall may be caused.

[0094] Moreover, in the development method of this invention, since fogging \*\*\*\* voltage (Vback) can be made low, consequently primary electrification of a photo conductor can be lowered by using the binary system developer of this invention which was described previously and which is charged good, the reinforcement of the photo conductor life can be carried out. Although Vback is based also on a development system in the development method of this invention, it is less than [ 100V ] more preferably below 150V. As contrast potential, 200V or 500V are preferably used so that picture concentration may come out enough.

[0095] Moreover, although the frequency between the peaks of an alternating electric field is related also to process speed with a low from 500Hz, since charge pouring to a carrier takes place, quality of image may be reduced by disturbing carrier adhesion or a latent image. On the other hand, if it exceeds 10,000Hz, a quality-of-image fall may be caused, without the ability of a toner following in footsteps to electric field.

[0096] Furthermore, in the development method of this invention, in order to perform development which takes out sufficient picture concentration, and is excellent in dot repeatability, and does not have carrier adhesion, contact width of face with the photo conductor drum 3 of the magnetic brush on the development sleeve 1 and the development nip C are important, and it is desirable in this invention to set the development nip C to 3 or 8mm. That is, if the value of the development nip C is narrower than 3mm, from 8mm, sufficient picture concentration and dot repeatability cannot be satisfied good, but the packing of latus and a developer breaks out, operation of a machine will be stopped and, even in \*\*, \*\*\*\*\*\* will fully become difficult about carrier adhesion. What is necessary is to adjust the distance A of the developer specification-part material 2 and the development sleeve 1 which were shown in drawing 1 as the adjustment method of the development nip C, or just to adjust nip width of face suitably by adjusting the distance B of the development sleeve 1 and a photoconductor drum 3. [0097] Next, the image formation method of this invention that the development method of this

invention which was described above is used is explained. Since there is no influence of a magnetic brush and a latent image is not disturbed by combining with the development system in which the digital latent image was formed still more preferably in the output of a full color picture which thinks especially a halftone as important using the binary system developer and the development method of this invention which were mentioned above according to the image formation method of this invention, faithful development is attained to a dot latent image, and formation of a high-definition picture is attained. Moreover, since the toner which has the sharp particle size distribution into which fines were cut also in imprint process is used according to the image formation method of this invention, high definitionization which can attain the rate of a high imprint, consequently can set the halftone section and the solid section can be attained. since [ furthermore, ] according to the image formation method of this invention the share concerning the developer within a development counter is small and can be managed with using the binary system developer of this invention which combined with early high definition-ization and was excellent in durability -- many -- the effect of this invention that there are few quality-of-image falls also in the copy of several sheets is fully acquired

[0098] above -- it excelled -- in the image formation method of this invention that an effect is demonstrated, the shape of surface type of a developer support is characterized by satisfying the following conditions

0.2 micrometer <= center line average coarseness -- the average of (Ra) <=5.0micrometer10micrometer<= irregularity -- Ra and Sm in the (interval Sm) <=80-micrometer0.05 <=Ra/Sm<=0.5 above-mentioned formula -- JIS B 0601 and ISO the center line average coarseness indicated by 468 -- and it is the value which specifies a concavo-convex average interval, and these are called for by the following formula (refer to the 3rd view) [0099]

中心線平均粗き: $Ra = (1/\ell) \int_0^\ell |f(x)| dx$ 凹凸の平均間隔: $Sm = (1/n)\sum\limits_{i=1}^{n} Sm_{i}$ 

式中、f(x): 測定方向をx軸

中心線を0とした時の粗さをy軸とした時の粗さ曲線

: 測定長さ Sm; : 凹凸間隔

[0100] If the value of Ra is smaller than 0.2 micrometers in above center line average coarseness, since the conveyance nature of a developer is inadequate, it will become easy to generate the picture unevenness and the concentration unevenness of a picture by durability. On the other hand, since the restraining force in the amount specification parts of developer conveyances, such as a blade, will become large too much although excelled in the conveyance nature of a developer if the value of Ra exceeds 5 micrometers, in response to degradation according [ an external additive ] to \*\*\*\*, the quality of image at the time of durability becomes easy to deteriorate.

[0101] If the value of the concavo-convex average interval Sm becomes larger than 80 micrometers, since the developer to a developer support top will become is hard to be held, picture concentration will become low. It is thought that it is to act as a lump with which packing of the developer was densely carried out when the interval of irregularity since slipping with a developer support has happened by the amount specification part of conveyances of as opposed to [ although the detail about the cause which the value of Sm contributes to this phenomenon is unknown, when the value of Sm becomes large 80 micrometers ] a developer support etc. became large too much, and for the force to exceed the holding power between a developer support and a developer. On the other hand, since many of irregularity of a developer support body surface becomes it smaller than a developer mean particle diameter that the value of Sm is less than 10 micrometers, grain-size selectivity arises in the developer which enters a crevice, and it becomes easy to generate weld by the developer fines component. Moreover, it is difficult also in manufacture to set a concavo-convex average interval to less than 10 micrometers.

[0102] Furthermore, when the uneven inclination (f\*\* (Ra/Sm)) called for from the height of the heights on a developer support and a concavo-convex interval is this invention, it becomes an important element from the above-mentioned viewpoint. That is, in the image formation method of this invention, an uneven inclination considers as the being [it/0.05 <=Ra/Sm<=0.5] feature. Moreover, in this invention, it is 0.07 <=Ra/Sm<=0.3 more preferably. Since the holding power to the developer support top of a developer becomes it weak that the value of Ra/Sm is less than 0.05 and a developer becomes is hard to be held to a developer support, the amount of conveyances becomes is hard to be controlled by the developer specification part, and picture unevenness arises as a result. If the value of Ra/Sm exceeds 0.5, it will be hard coming to circulate the developer included in the crevice of a developer support body surface with other developers, and developer weld will occur. In addition, measurement of Ra in this invention and Sm was performed based on JIS-B0601 using contact process surface roughness measuring instrument SE-3300 (the Kosaka lab company make).

[0103] In the image formation method of this invention, it is desirable to use the \*\*\*\*\*\*\*\* thing which has the irregular surface roughness which satisfies the requirements which the front face described above as a developer support, and a regular slot prepares in the direction of a major axis of a developer support further. That is, it becomes easy to coat a developer support body surface with a developer by making several slots (the so-called knurling tool) process it in the length direction of a developer support uniformly, when the developer which was further excellent in the fluidity is used. [0104] The sandpaper method for grinding a sleeve side against the sandpaper for forming irregularity in the sandblasting method and sleeve circumferencial direction which used the indeterminate form and the fixed form particle as an abrasive grain, for example as a method of manufacturing the developer support which has the predetermined surface roughness used in the image formation method of this invention at shaft orientations, the method by the chemical treatment, the method of forming after [ a coat ] resin heights by the elastic resin, etc. can be used.

[0105] As a formation material of a developer support used in this invention, all well-known material can be used conventionally. For example, the thing which processed into rubber, the firing object, and the sponge form elastic bodies, such as what covered carbon, the resin elastomer, etc. on metals, such as aluminum, stainless steel, and nickel, or these metals, natural rubber, silicone rubber, polyurethane rubber, and neoprene rubber, or the thing which applied carbon, the resin elastomer, etc. on these elastic bodies is mentioned. Moreover, as a configuration, each well-known form, such as the shape of the shape of a cylinder and a sheet, can use it for a developer support conventionally.

[0106] Hereafter, the measuring method of the various physical-properties values used in this invention is indicated. First, the measuring method of a magnetic carrier particle size used by this invention is indicated. That is, although regulated by the number mean particle diameter, as the measuring method, the particle size of a carrier extracted 300 or more carrier particles at random with the optical microscope, with the image-processing analysis equipment Luzex3 made from NIREKO, it had horizontal Ferre, measured it as a carrier particle size, and computed the number mean particle diameter using the obtained carrier particle size. Furthermore, from the particle size distribution of the number criteria measured on this condition, the accumulation rate below 1 / diameter cumulative distribution of double precision of a number mean particle diameter (D1) was searched for, and the accumulation value below 1 / diameter cumulative distribution of double precision was calculated.

[0107] The magnetic properties of the carrier used by this invention were measured using oscillating magnetic field mold magnetic-properties automatic-arrangement-for-recording BHV-30 made from \*\*\*\* Electron. That is, the magnetic-properties value of carrier fine particles made the external magnetic field of a 1K oersted, and asked for the intensity of magnetization at that time. Under the present circumstances, the carrier used for the measurement sample is changed into the state where packing was carried out so that it might become sufficiently dense at the plastic envelope of the shape of a cylinder of the about 0.07 cm volume 3, and is produced.

[0108] The magnetization moment is measured in this state, the actual weight when paying a sample is measured, and it asks for intensity of magnetization (emu/g). Subsequently, it asks for the true specific gravity of a carrier particle with the dry type automatic density meter AKYU pick 1330 (Shimadzu

[ Corp. ] Corp. make), and asks for the intensity of magnetization (emu/cm3) per [ which is used by this invention by applying true specific gravity to intensity of magnetization (emu/g) ] unit area. [0109] In this invention, specific resistance measurement of a magnetic carrier was performed using the measuring device shown in drawing 2. Cell E was filled up with the carrier, test sample was created, electrodes 21 and 22 were allotted and voltage was impressed to inter-electrode so that a restoration carrier might be touched, and it asked for specific resistance by measuring the current which flows then. In the above-mentioned measuring method, since a carrier is powder, change may arise in a filling factor and specific resistance may change in connection with it in case test sample is created, cautions are required. as the measurement conditions for the used specific resistance in this invention -- touch-area S= of a restoration carrier and an electrode -- about 2.3 -- cm2 and thickness -- it was referred to as 180g of loads of d = about 2mm and the up electrode 22, and applied-voltage 100V [0110] Moreover, the particle-size measuring method of a metallic oxide used as a component of the magnetic carrier used by this invention is indicated below. Using the photograph expanded by 5,000 or 20,000 times with the scanning electron microscope S-4500 by Hitachi [, Ltd. ], Ltd., the number mean particle diameter of a metallic oxide extracted 300 or more metallic-oxide particles at random, and it computed the number mean particle diameter with the image-processing analysis equipment Luzex3 made from NIREKO by having had horizontal Ferre, having measured as a metallic-oxide particle size,

[0111] Furthermore, specific resistance measurement of a metallic oxide was performed according to the above-mentioned method of magnetic carrier specific resistance. That is, the cell E of <u>drawing 2</u> was filled up with the metallic-oxide particle, test sample was created, electrodes 21 and 22 were allotted so that a restoration metallic oxide might be touched, voltage was impressed to this inter-electrode one, and it asked for specific resistance by measuring the current which flows then. It is filled up making right and left rotate the up electrode 21 so that an electrode may contact uniformly to test sample on the occasion of restoration of a metallic oxide. as the measurement conditions for the specific resistance of the metallic oxide in the above-mentioned measuring method -- touch-area S= of a restoration metallic oxide and an electrode -- about 2.3 -- cm2 and thickness -- it was referred to as 180g of loads of d = about 2mm and the up electrode 22, and applied-voltage 100V

[0112] The metallic-oxide average exposure density in the carrier front face of the coat magnetism carrier particle used in this invention measured the photograph (1kV of acceleration voltage) by the scanning electron microscope S-4500 (Hitachi, Ltd. make) expanded by 5,000 or 10,000 times using image-processing analysis equipment Luzex3 (product made from NIREKO). Namely, carrier particle 1 It observed with the scanning electron microscope from the perpendicular upper part about the individual, and the exposure number of the metallic oxide per unit area was counted and computed in two dimensions about the carrier particle table semi-sphere. The above-mentioned operation was repeated in this invention, 300 or more carrier particles were extracted at random, equalization processing was performed, and the metallic-oxide exposure density in a carrier front face was measured.

[0113] In the molecular weight distribution by GPC of the THF extractives of the toner of this invention, GPC (gel permeation chromatography) by Showa Denko K.K. was used for measurement of the maximum peak of molecular weight, and the content of a with a molecular weight of 1000 or less component. In a column, it is Polymer. Laboratories Using THF in PLge110micromMIXED-B made from Ltd., and a solvent, the rate of flow was performed by 1.0 ml/min, and temperature was performed on 40-degree C conditions. The calibration curve was produced by the mono dispersion polystyrene standard sample. Molecular weight distribution used the thing of weight criteria. A sample is created as follows. It fully shakes, after paying a sample into THF and leaving it for several hours, THF is mixed well (until the coalescence object of a sample is lost), and it puts for further 12 hours or more. It is made for the neglect time to the inside of THF to turn into 24 hours at this time. Then, let what passed the sampling processing filter (pore size 0.45 or 0.5micrometer., for example, my SHORI disk H-25-5 TOSOH CORP. make, and made in EKIKURO disk 25CR germane science Japan can be used) be the sample of GPC. Sample concentration is adjusted so that a resinous principle may become in 0.5 or ml

and having carried out equalization processing.

and 5mg/.

[0114] The example of the mean particle diameter and the measuring method of particle-size-distribution measurement of a toner is shown. Using the photograph of the toner expanded by 500 or 5000 times with the scanning electron microscope S-4500 by Hitachi [, Ltd. ], Ltd., a toner particle with a radius of 0.1 micrometers or more is extracted 300 or more pieces at random, with the image-processing analysis equipment Luzex3 made from NIREKO, it has a diameter of a horizontal fillet, and measures as a toner particle diameter, and particle-size-distribution data are obtained. The number mean particle diameter (D1) and the volume mean particle diameter (D3) were computed by computer-processing from there, and the coefficient of variation of the particle size distribution of number criteria was computed by breaking the standard deviation of the particle size distribution of the distribution accumulation value of the toner particle below the diameter of 1-/double precision of a number mean particle diameter (D1) and the distribution accumulation value of the toner particle more than the diameter of double precision of a volume mean particle diameter (D3), and number criteria by the number mean particle diameter.

[0115] It asks for the number mean particle diameter measured on this condition, and also a volume mean particle diameter by computer-processing. From the particle size distribution of the acquired number criteria, the accumulation rate below the diameter cumulative distribution of 1-/double precision of a number mean particle diameter (D1) is calculated, and the accumulation value below the diameter cumulative distribution of 1-/double precision is calculated. Similarly, from the particle size distribution of volume criteria, the accumulation rate more than the diameter cumulative distribution of double precision of a volume mean particle diameter (D3) is calculated, and the accumulation value more than the diameter cumulative distribution of double precision is calculated.

[0116] Next, the measuring method of the amount of triboelectrification of the developer used by this invention is indicated. A toner and a carrier are mixed so that a toner weight may become 5 % of the weight, and it mixes for 60 seconds with a turbular mixer, and the carrier for measurement is created. This developer is put into the metal container which equipped the pars basilaris ossis occipitalis with the conductive screen of 500 meshes, and the amount of triboelectrification is calculated from the potential accumulated at the capacitor which drew in with the suction machine and was connected to the weight difference before and behind suction, and the container. Suction force in this case was set to 250mmHg (s) in this invention. The amount of triboelectrification is computed using the following formula from the value acquired by the above-mentioned method.

 $Q(\text{muC/g}) = (\text{CxV}) \times (\text{W1-W2}) - 1$  (W1 is the weight of the developer before suction among a formula, W2 is a weight after suction, and it is the potential by which C was accumulated at the capacity of a capacitor and V was accumulated at the capacitor.)

[Example] Hereafter, an example and the example of comparison are given and this invention is explained still more concretely. In addition, this invention is not restricted by the example. First, example A-H of manufacture for obtaining toner A-H used in the example and the example of comparison of this invention is listed below.

[0118]

[The example A of manufacture of a toner]

- Polyvinyl methyl ether 20 weight sections and methanol 130 weight \*\*\*\*\* and the above-mentioned prescription were put into the reaction container furnished with a thermometer, churning equipment, and the reflux condenser, and were enough agitated at the room temperature under the nitrogen air current.
- Styrene 25 weight sections and n-butyl acrylate 6 weight sections and a copper-phthalocyanine pigment The 1.5 weight section and salicylic-acid metallic compounds 1 weight section, 2, and 2-azobisisobutyronitril 2 weight sections, next the above-mentioned prescription are agitated enough, and after carrying out the mixed dissolution, it heated at 65 degrees C and was made to react under a nitrogen air current for 15 hours in addition to the inside of a previous reaction container. And the obtained reactant was filtered, and after carrying out methanol dilution and fully agitating \*\*\*\*, this was filtered again. This operation was repeated several times. Obtained \*\*\*\* was fully dried with the

vacuum dryer, and the toner particle was obtained.

[0119] About 4.5 micrometers (D3) of volume mean particle diameters and the number mean particle diameter (D1) were 3.8 micrometers, the distribution accumulation value below the diameter of 1-/double precision of a number mean particle diameter was several 0%, and the distribution accumulation value more than the diameter of double precision of a volume mean particle diameter of the toner particle obtained above was 0 volume %. The coefficient of variation of the particle size distribution of number criteria was 7.8%. Moreover, shape factor SF-1 of a toner was 110. In the molecular weight distribution by GPC of the THF extractives of a toner particle, the peak (Mp) of molecular weight was 8,200, and the content of a with a molecular weight of 1,000 or less molecule was 0.0 % of the weight on the basis of the weight of a toner particle. Furthermore, the silica pulverized-coal 2 weight section of 0.04 micrometers of number mean particle diameters which carried out hydrophobing processing by the hexamethyldisilazane was mixed by the Henschel mixer to the toner particle 100 weight section obtained above, and the outside \*\* toner A was obtained. The external additive coverage of the outside \*\* toner A was 70%.

[0120]

[The example B of manufacture of a toner]

- Polyvinyl methyl ether 20 weight sections and methanol 130 weight \*\*\*\*\* and the above-mentioned prescription were put into the reaction container furnished with a thermometer, churning equipment, and the reflux condenser, and it agitated enough at the room temperature under the nitrogen air current. - Styrene 27 weight sections and n-butyl acrylate 3 weight sections and salicylic-acid metallic compounds 1 weight section, 2, and 2-azobisisobutyronitril 2 weight sections, next the above-mentioned prescription are agitated enough, and after carrying out the mixed dissolution, it heated at 65 degrees C and was made to react under a nitrogen air current for 15 hours in addition to the inside of a previous reaction container. And the obtained reactant was filtered, and after diluting \*\*\*\* with the methanol in which the oil red 6 weight section was dissolved and fully agitating it, this was filtered again. The colored filtration object was diluted with the methanol and operation of filtering was repeated several times. Obtained \*\*\*\* was fully dried with the vacuum dryer, and the toner particle was obtained. [0121] About 5.1 micrometers (D3) of volume mean particle diameters and the number mean particle diameter (D1) were 4.5 micrometers, the distribution accumulation value below the diameter of 1-/double precision of a number mean particle diameter was several 0%, and the distribution accumulation value more than the diameter of double precision of a volume mean particle diameter of the toner particle obtained above was 1 volume %. The coefficient of variation of the particle size distribution of number criteria was 8.2%. Moreover, shape factor SF-1 of a toner was 115. In the molecular weight distribution by GPC of the THF extractives of a toner particle, the peak (Mp) of molecular weight was 9,100, and the content of a with a molecular weight of 1,000 or less molecule was 0.5 % of the weight on the basis of the weight of a toner particle. Furthermore, further, to the toner particle 100 weight section obtained above, the titanium oxide pulverized-coal 2 weight section of 0.03 micrometers of number mean particle diameters which carried out hydrophobing processing by the silane system coupling agent was mixed by the Henschel mixer, and the outside \*\* toner B was obtained. The external additive coverage of the outside \*\* toner B was 65%. [0122]

[The example C of manufacture of a toner]

- Polyvinyl pyrrolidone 15 weight sections and methanol 150 weight \*\*\*\*\* and the above-mentioned prescription were put in the reaction container furnished with a thermometer, churning equipment, and the reflux condenser, and were enough agitated at the room temperature under the nitrogen air current.
- Styrene 17 weight sections and ethyl methacrylate 17 weight sections and a copper-phthalocyanine pigment The 1.5 weight section and salicylic-acid metallic compounds 1 weight section, 2, and 2azobisisobutyronitril 2 weight sections, next the above-mentioned prescription are agitated enough, and after carrying out the mixed dissolution, it heated at 65 degrees C and was made to react under a nitrogen air current for 15 hours in addition to the inside of a previous reaction container. And the obtained reactant was filtered, and after diluting \*\*\*\* with the methanol and fully agitating it, this was

filtered again. This operation was repeated several times. Obtained \*\*\*\* was fully dried with the vacuum dryer, and the toner particle was obtained.

[0123] About 4.8 micrometers (D3) of volume mean particle diameters and the number mean particle diameter (D1) were 4.2 micrometers, the distribution accumulation value below the diameter of 1-/double precision of a mober mean particle diameter was several 2%, and the distribution accumulation value more than the dimeter of double precision of a volume mean particle diameter of this obtained toner particle was 2 volume %. The coefficient of variation of the particle size distribution of number criteria was 16.0%. Moreover, shape factor SF-1 was 129. In the molecular weight distribution by GPC of the THF extractives of a toner particle, the peak (Mp) of molecular weight was 7,200, and the content of a with a molecular weight of 1,000 or less molecule was 2.1 % of the weight on the basis of the weight of a toner particle. Furthermore, the silica pulverized-coal 2.5 weight section of 0.05 micrometers of number mean particle diameters which carried out hydrophobing processing by the hexamethyldisilazane was mixed by the Henschel mixer to the toner particle 100 weight section obtained above, and the outside \*\* toner C was obtained. The external additive coverage of the outside \*\* toner C was 75%.

[0124]

[Manufacture D of a toner]

- Polyvinyl alcohol 20 weight sections and methanol 120 weight \*\*\*\*\* and the above-mentioned prescription were put into the reaction container furnished with a thermometer, churning equipment, and the reflux condenser, and were enough agitated at the room temperature under the nitrogen air current. - Styrene 18 weight sections and ethyl methacrylate 15 weight sections and salicylic-acid metallic compounds 1 weight section, 2, and 2-azobisisobutyronitril 2 weight sections, next the above-mentioned prescription are agitated enough, and after carrying out the mixed dissolution, it heated at 65 degrees C and was made to react under a nitrogen air current for 15 hours in addition to the inside of a previous reaction container. And the obtained reactant was filtered, and after diluting \*\*\*\* with the methanol in which the oil black 6 weight section was dissolved and fully agitating it, this was filtered again. The colored filtration object was diluted with the methanol and operation of filtering was repeated several times. Obtained \*\*\*\* was fully dried with the vacuum dryer, and the toner particle was obtained. [0125] About 7.1 micrometers (D3) of volume mean particle diameters and the number mean particle diameter (D1) were 6.3 micrometers, the distribution accumulation value below the diameter of 1-/double precision of a .umber mean particle diameter was several 4%, and the distribution accumulation value more than the diameter of double precision of a volume mean particle diameter of this obtained toner particle was 5 volume %. The coefficient of variation of the particle size distribution of number criteria was 18.2%. Moreover, shape factor SF-1 was 131. In the molecular weight distribution by GPC of the THF extractives of a toner particle, the peak (Mp) of molecular weight was 22,000, and the content of a with a molecular weight of 1,000 or less molecule was 2.0 % of the weight on the basis of the weight of a toner particle. Furthermore, the silica pulverized-coal 2 weight section of 0.06 micrometers of numbe mean particle diameters which carried out hydrophobing processing by the hexamethyldisilazane as mixed by the Henschel mixer to the toner particle 100 weight section obtained above, and the outside \*\* toner D was obtained. The external additive coverage of the outside \*\* toner D was 60%.

[0126]

[The example E of mainfacture of a toner]

- Polyvinyl methyl ether 20 weight sections and methanol 130 weight \*\*\*\*\* and the above-mentioned prescription were put if to the reaction container furnished with a thermometer, churning equipment, and the reflux condenser, and divergence weight agreement and the reflux condenser, and divergence weight agreement and the reflux condenser. The divergence weight sections and weight sections and N-butyl acrylate 9 weight sections and a copper-phthalocyanine pigment. The 2.5 weight sections and salicylic-acid metallic compounds 2 weight sections, 2, and 2-azobisisobutyronitril 4 weight sections, next the above-mentioned prescription are agitated enough, and after carrying out the mixed dissolution, it heated at 65 degrees C and was made to react under a nitrogen air current for 15 hours in addition to the inside of a previous reaction container. And the

obtained reactant was filtered again. T vacuum dryer, a [0127] About 5.0 mic diameter (D1) were 4. distribution of rumb weight was 12,0 the weight on the

Itered, and after diluting \*\*\*\* with the methanol and fully agitating it, this was ation was repeated several times. Obtained \*\*\*\* was fully dried with the oner particle was obtained.

meters (D3) of volume mean particle diameters and the number mean particle micrometers, the distribution accumulation value below the diameter of 1-/double precision of a number mean particle diameter was several 12%, and the distribution accumulation value more than the diameter of double precision of a volume mean particle diameter of this obtained toner p. icle was 13 volume %. The coefficient of variation of the particle size criteria was 26.6%. Moreover, shape factor SF-1 was 109. In the molecular weight distribution in JPC of the THF extractives of a toner particle, the peak (Mp) of molecular the content of a with a molecular weight of 1,000 or less molecule was 8.0 % of of the weight of a toner particle. Furthermore, the silica pulverized-coal 2 weight section of 0.04 m crometers of number mean particle diameters which carried out hydrophobing processing by the hexamethyldisilazane was mixed by the Henschel mixer to the toner particle 100 weight section obtained above, and the outside \*\* toner E was obtained. The external additive coverage of the outside \*\* toner E was 70%.

[0128]

[The example F of my infacture of a toner]

tion of the 180 weight sections and polyvinyl alcohol 20 weight \*\*\*\*\* and the - Water 0.2wt(s above-mentione ore iption were put into the 4 mouth flask, and it put into the reaction container furnished with charm. equipment and the reflux condenser, and agitated enough at the room temperature under the nitrogen air current.

- Styrene 77 weight sections and acrylic-acid-n-butyl 22 weight sections and benzoyl peroxide The 1.4 weight section and divinylbenzene The 0.2 weight sections, next the above-mentioned prescription were agitated enough, and after carrying out the mixed dissolution, in addition to the inside of a previous reaction container, it agitated under the nitrogen air current and considered as suspension. Then, the temperature up ried out to 80 degrees C, it held at this temperature for 10 hours, polymerization reaction was perform and the polymer was obtained.

ture at 65 degrees C, after rinsing this obtained polymer, it dried in the reduced [0129] **Keeping** m pressure environment and the resin was obtained. This resin was mixed by 88 weight sections, 2 weight sections and the carbon black 5 weight section were mixed for metal-containing azo dye with the fixed tub type dry-blending machine, having connected with the suction pump and attracting a vent-port, the 2 shaft extruder performed melting kneading and the melting kneading object was obtained. Coarse grinding of this me'ting kneading object was carried out with the hammer mill, and the crushing object of the toner covered tof 1mm mesh path was obtained. Furthermore, after the jet mill which used the collision betwe es in a revolution style after the mechanical grinder ground this crushing object to 20-30 micron. er. volume mean diameters ground, the multi-stage rate classifier performed the classification and the lack toner particle was obtained.

[0130] About 4.5 micrometers (D3) of volume mean particle diameters and the number mean particle diameter (D1) ware 4 i micrometers, the distribution accumulation value below the diameter of 1-/double precisic of a number mean particle diameter was several 8%, and the distribution accumulation value more than the sameter of double precision of a volume mean particle diameter of this obtained Nume %. The coefficient of variation of the particle size distribution of number toner particle v eover, shape factor SF-1 was 148. In the molecular weight distribution by GPC criteria was 19 cf a toner particle, the peak (Mp) of molecular weight was 62,000, and the of the THF ext content of a witt cular weight of 1,000 or less molecule was 6.3 % of the weight on the basis of ticle. Furthermore, the silica pulverized-coal 2.5 weight section of 0.05 the weight of a: nean particle diameters which carried out hydrophobing processing by the micrometers of e was mixed by the Henschel mixer to the toner particle 100 weight section hexamethyldisi' e outside \*\* toner F was obtained. The external additive coverage of the outside obtained above \*\* toner F was

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[0131]
 The example
                       ir facture of a toner]
                       v sight sections and methanol 140 weight ***** and the above-mentioned
 - Polyvinyl ph-
                         o the reaction container furnished with a thermometer, churning equipment, and
 prescription we
 the reflux cond
                      and were enough agitated at the room temperature under the nitrogen air current.
 - Styrene 25 w
                  h: ections and 2-ethylhexyl acrylate 5 weight sections and the C.I. pigment red 122
                     on and salicylic-acid metallic compounds 1 weight section, 2, and 2-
 The 1.5 weight.
 azobisisobutyroi ti. 2 weight sections, next the above-mentioned prescription are agitated enough, and
 after carrying our thin mixed dissolution, it heated at 65 degrees C and was made to react under a
 nitrogen air curr
                      or '5 hours in addition to the inside of a previous reaction container. And this
                       fi tered, and after carrying out methanol dilution and fully agitating ****, this was
 obtained react:
 filtered again.
                       tion was repeated several times. Obtained **** was fully dried with the
 vacuum dryer.
                       'ner particle was obtained.
 [0132] About
                      rometers (D3) of volume mean particle diameters and the number mean particle
 diameter (D1)
                  re > 5 micrometers, the distribution accumulation value below the diameter of 1-
                     a number mean particle diameter was several 7%, and the distribution accumulation
 double precision
 value more than he diameter of double precision of a volume mean particle diameter of this obtained
                  I volume %. The coefficient of variation of the particle size distribution of number
 toner particle we
                       orcover, shape factor SF-1 was 121. In the molecular weight distribution by GPC
 criteria was 18
 of the THF ext
                      of a toner particle, the peak (Mp) of molecular weight was 8,900 and the content
 of a with a mo
                       veight of 1,000 or less molecule was 6.0 % of the weight on the basis of the
 weight of a tor
                       cle. Furthermore, the silica pulverized-coal 2 weight section of 0.05 micrometers
                  retucle diameters which carried out hydrophobing processing by the silane system
 of number me
                    mixed by the Henschel mixer to the toner particle 100 weight section obtained
 coupling agent v
 above, and the o 's de ** toner G was obtained. The external additive coverage of the outside ** toner
 G was 55%.
[0133]
The example of
                       nufacture of a toner]
                       he 240 weight section and 0.1 M-Na3PO4 After mixing 150 weight ***** and
- Ion exchange 'a'
                       rescription and warming at 60 degrees C, it agitated in rotational frequency
the above-mer
                    cormula homomixer (product made from special opportunity-ized industry). The
12,000rpm us<sup>1</sup>
1.0 M-CaCl2 sc
                   on 23 weight section was gradually added to this, and the drainage system medium
containing calci
                   3 (P( ↓) was obtained.
                    sections and n-butyl acrylate 11 weight sections and the C.I. pigment blue 15:3 5
- Styrene 55 wc
                     ticylic-acid metallic compounds After mixing 1 weight section, next the above-
weight section and
                      and warming at 60 degrees C, it agitated in rotational frequency 12,000rpm
mentioned pre rij
                       omixer (product made from special opportunity-ized industry). Supplying in the
using TK form
drainage syste
                       n produced by the above, agitating for 10 minutes by 10,000rpm by TK formula
homomixer u
                        rees C and a nitrogen air current, and agitating by the paddle impeller after that,
                  e 2 and 2-azobisisobutyronitril 3 weight section in this, the temperature up was carried
after dissolvir
                  C, and polymerization reaction was carried out to them for 10 hours. After the
out to 80 degr
                  ection and, after distilling off the residual monomer, cooling under reduced pressure,
polymerizatio -
                   low icid and dissolving calcium phosphate, it filtered, rinsed and dried and the toner
adding the hve
particle was c
                ij
[0134] About
                         eters (D3) of volume mean particle diameters and the number mean particle
                ) j
                       micrometers, the distribution accumulation value below the diameter of 1-
diameter (D1)
/double preci-
                        mber mean particle diameter was several 7%, and the distribution accumulation
                  ٠، اد
value more t
                 ιe d
                         cter of double precision of a volume mean particle diameter of this obtained
toner particle
                        me %. The coefficient of variation of the particle size distribution of number
                  3 v
criteria was
                         over, shape factor SF-1 was 135. In the molecular weight distribution by GPC
                 5. M
of the THF ex
                         a toner particle, the peak (Mp) of molecular weight was 12,000, and the
                  ive
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h a m cular weight of 1,000 or less molecule was 15.3 % of the weight on the basis of content of a v the weight of 'one" rticle. Furthermore, the silica pulverized-coal 2.5 weight section of 0.05 micrometers mean particle diameters which carried out hydrophobing processing by the nu silane syster uplin ent was mixed by the Henschel mixer to the toner particle 100 weight section and th utside \*\* toner H was obtained. The external additive coverage of the outside obtained abo \*\* toner H v <sup>-</sup>5%. [0135] [The examp] of mar icture of a toner eight sections and methanol 140 weight \*\*\*\*\* and the above-mentioned ol 22 - Polyvinyl r prescription v 2 m. " to the reaction container furnished with a thermometer, churning equipment, and the reflux con ns were enough agitated at the room temperature under the nitrogen air current. - Styrene 24 of ts ons and n-butyl acrylate 6 weight sections and the C.I. pigment blue 15:3 The icylic-acid metallic compounds 1 weight section, 2, and 2-1.5 weight s r an azobisisobu<sup>\*</sup> ∵ril 2 sight sections, next the above-mentioned prescription are agitated enough, and after carryin the r red dissolution, it heated at 65 degrees C and was made to react under a 5 hours in addition to the inside of a previous reaction container. This obtained nitrogen air int for after carrying out methanol dilution and fully agitating \*\*\*\*, this was filtered reactant was ^ered. a again. This co rtion is repeated several times. Obtained \*\*\*\* was fully dried with the vacuum dryer, ti ' s obtained. and the tone: [0136] Abo teters (D3) of volume mean particle diameters and the number mean particle diameter (D 3 6 icrometers, the distribution accumulation value below the diameter of 1-/double prec ١f a aber mean particle diameter was several 7%, and the distribution accumulation value more re d₁ eter of double precision of a volume mean particle diameter of this obtained toner particl < 1 vc ne %. The coefficient of variation of the particle size distribution of number criteria was 3%. M over, shape factor SF-1 was 120. In the molecular weight distribution by GPC of the THF ctives of a toner particle, the peak (Mp) of molecular weight was 8,900, and the content of a with a r ч ч, ght of 1,000 or less molecule was 4.5 % of the weight on the basis of the · ti weight of a Furthermore, the silica pulverized-coal 2 weight section of 0.05 micrometers of number 1 liameters which carried out hydrophobing processing by the silane system coupling ag by the Henschel mixer to the toner particle 100 weight section obtained 17 above, and. id toner I was obtained. The external additive coverage of the outside \*\* toner I was 55%. [0137] Next e exan s 1-6 of manufacture for obtaining the carriers 1-6 used in the example and the example of this invention are given below. arisc To alpha-Fe shms of specific resistance (cm)) of the magnetite (6x105ohms of specific  $\chi 1$ resistance (c) 1.2 icrometers of the [example 1 of manufacture of carrier] number mean particle meters of number mean particle diameters, 3-(2-aminoethyl aminopropyl) diameters, a dimethoxys a silane system coupling agent was added 5.5% of the weight, respectively, high-speed ni ing was carried out at the temperature of 100 degrees C or more within the ( churning conta pophilic-ized processing of each metallic-oxide particle , ai [0138] : •ht - A phenol 10 ions and a formaldehyde solution (formaldehyde 40% and methanol 10% and water 50%) T )1 :--ization[ 6 weight sections and ]-processed magnetite Lipophilic--ization[ 40 weight sect of 7: cessed alpha-Fe 2O3 A temperature up is carried out to 85 degrees C in 40 minutes, ag xing [ put aqueous ammonia and water into a flask 28%, ] with the material of 60 weight s this temperature was held and 3-hour reaction and hardening of were done. Then, it conte ees C, and further, after adding water, the supernatant was removed. precipitate va ,ec ; it was air-dry. Subsequently, it dried at 50-60 degrees C under reduced pressure of thi (. mmHgs), and the particle of the magnetite and hematite which were lipophilicor l -ization-proce e obf d the spherical carrier core combined considering phenol resin as a binder. The specific r the obtained carrier core was 5.2x1011-ohmcm. ٠.

[0139] Furthermore, u the following methods magnetism carrier was silicone resin was prod particle front face mig' solution, applying sheat performed. After carry for 1 hour, it cracked, i [0140] thermosetting silicone resin, the coat of the silicone resin was carried out by he front face of the carrier core particle obtained above, and the resin coat tained on it. First, the carrier coat solution which has 10% of the weight of ed, using toluene as a solvent so that the amount of coat resins of a carrier core recome 1.0% of the weight. The solvent was volatilized using this coat g stress continuously, and the resin coat to a carrier core particle front face was out the cure of the obtained coat magnetism carrier particle at 200 degrees C lassified by the screen of 200 meshes, and the carrier 1 was obtained.

Since it became timeor

ime, translation result display processing is stopped.